Supporting Information

Synthesis and characterization of Ag-delafossites Ag*B*O_2 (B: Al, Ga, In) from rapid hydrothermal process

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S1 Sample overview

All samples prepared in this work are listed in the Table S1 – S3.

Table S1: Denomination of samples according to the investigated synthesis parameter. The internal sample identification numbers (ID_{FHI}) are given. Selected samples are part of several series (italic letters) or obtained applying the optimized reaction conditions (bold letters).

***B*: Al**			***B*: Ga**			***B*: In**		
Sample	ID_{FHI}		Sample	ID_{FHI}		Sample	ID_{FHI}	
	As prepared	After STA		As prepared	After STA		As prepared	After STA
Al_1eq	#29179		Ga_1eq	#27430		In_1eq	#27601	
Al_2eq	*#29180*		Ga_2eq	*#27429*		In_1.5eq	#27602	
Al_3eq	#29181		Ga_3eq	#27428		In_2eq	#27483	
Al_0.1M	#23236		Ga_30h	*#27429*		**In_1.4g**	#27626	#29288
Al_0.9M	*#29180*		Ga_20h	#27439		**3R-$AgInO_2$**		
Al_1.5M	#23660		**Ga_10h**	#27445	#29284			
Al_60h	*#29180*		**3R$AgGaO_2$**					
Al_45h	#29192							
Al_30h	#25158, #25552 (IR/Raman)	#29286						
3R-$AgAlO_2$								

Table S2: Hydrothermal synthesis time variation (t). Samples and internal sample identification numbers (ID_{FHI}) are given.

t [h]	ID_{FHI}	t [h]	ID_{FHI}
60	#29179	**14**	**#27430**
40	#29180	12	#27429
19	#29181	10	#27428
17	#23236	5	#27429
16	#29180	3	#27439
15.3	#23660		

Table S3: internal sample identification numbers (ID_{FHI}) of 3R-$AgAlO_2$ scale-up sample.

Sample	ID_{FHI}
Scale-up	**#27437**

S2 Synthesis of Ag delafossites

S2.1 3R-$AgAlO_2$

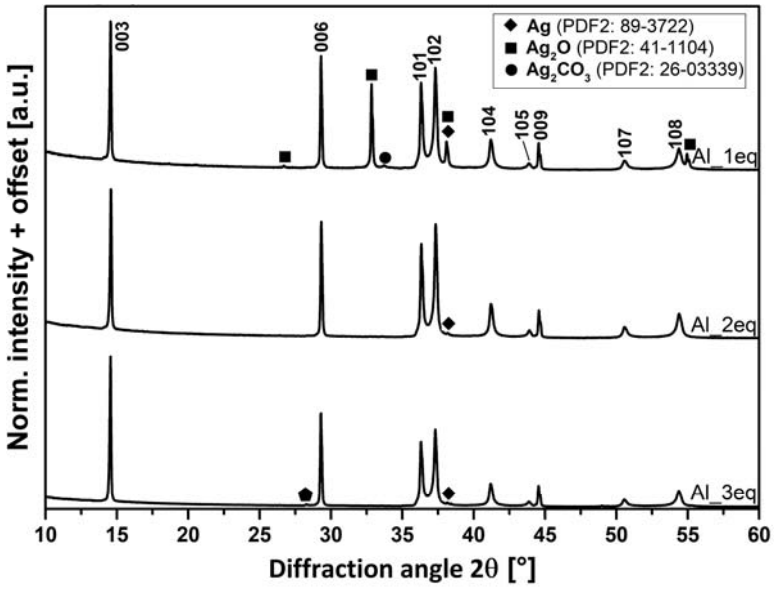

Figure S1: Powder XRD patterns of samples obtained by variation of educt ratios. Reflections of 3R-$AgAlO_2$ indexed.

Table S4: ICP-OES results of the after-reaction analysis of the colorless liquors of Al_1eq – Al_3eq.

Sample	ICP-OES analysis [mgl^{-1}]	
	Ag	Al
Al_1eq	15.43	4469
Al_2eq	9.608	7461
Al_3eq	8.502	8503

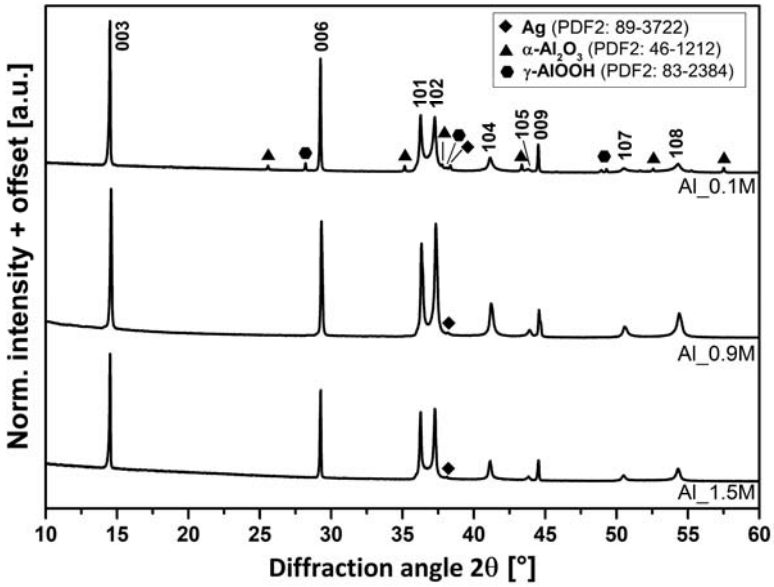

Figure S2: Powder XRD patterns of samples obtained by variation of NaOH concentration. Diffraction peaks of 3R-$AgAlO_2$ indexed.

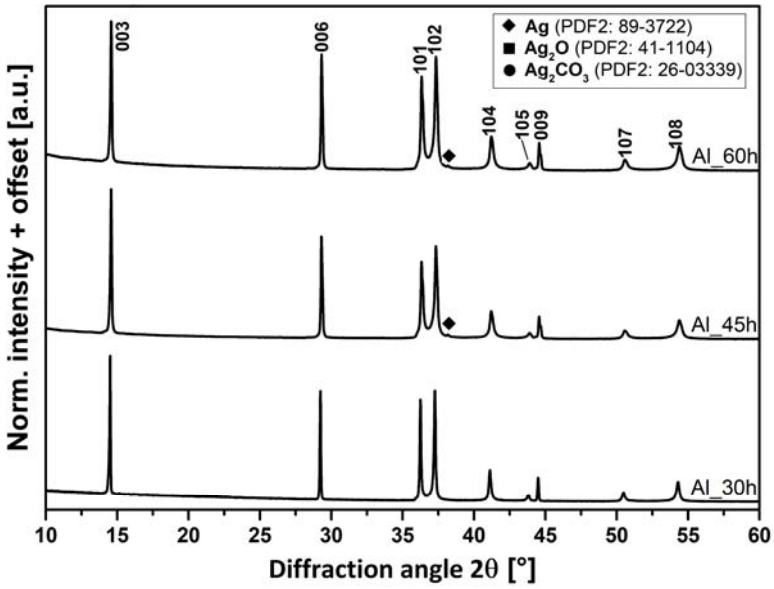

Figure S3: Powder XRD patterns of samples obtained by variation of the hydrothermal synthesis time. Reflections of crystallite main phase 3R-$AgAlO_2$ indexed.

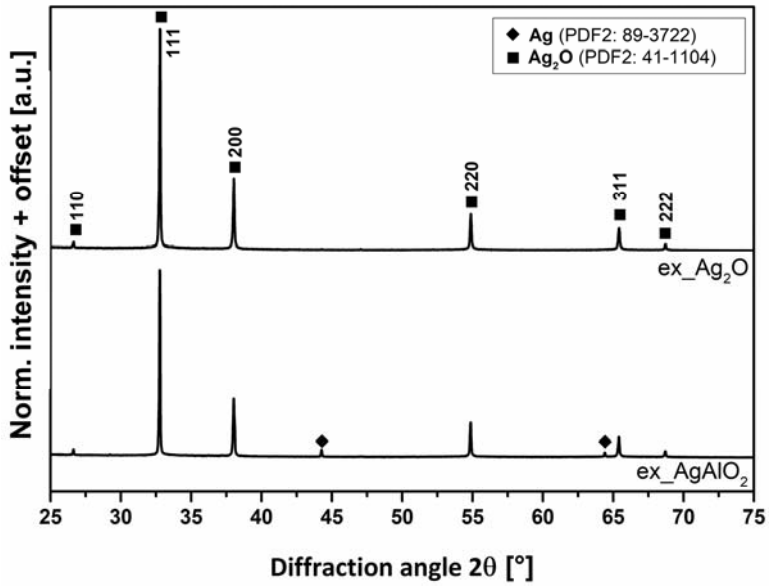

Figure S4: Powder XRD patterns of hydrothermally treated Ag_2O and 3R-$AgAlO_2$. Reflections of Ag_2O indexed.

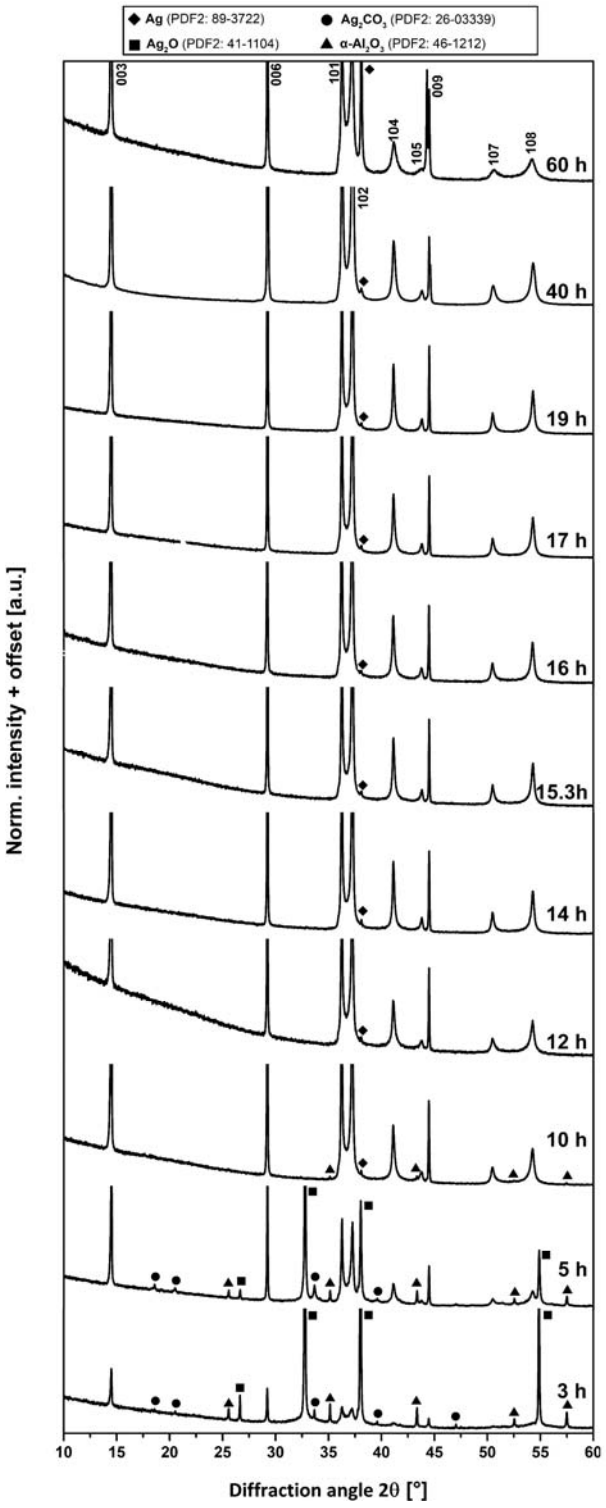

Figure S5: Powder XRD patterns of samples obtained by varying the reaction time from 60 h to 3h. 3R-$AgAlO_2$ reflections indexed.

For the hydrothermal synthesis a custom-made pressure reactor setup (Picoclave, Büchi) equipped with a 190 ml PTFE lined stainless steel pressure vessel was used. In a typical synthesis Ag_2O (4.043 g, 17.45 mmol, 1.0 eq, >99% Carl Roth) and α-Al_2O_3 (3.557 g, 34.89 mmol, 2.0 eq, 99+ %, 40 nm APS, Chempur) were mixed in an agate mortar and placed in the PTFE lined pressure vessel, which was then backfilled with NaOH solution (110 ml, 0.9 M, NaOH: >99 %, Carl Roth). The pressure vessel was sealed, and the PTFE stirrer was set up to 250 rpm. The reaction vessel was then heated to the desired reaction temperature of 483 K with a rate of 1.0 $Kmin^{-1}$. The maximum temperature was held constant for 3 h to 60 h. Pressurized air was used for a controlled cooling back to room temperature in > 90 min. After reaching room temperature, the polycrystalline product was recovered, washed and dried.

An increased amount of 3R-$AgAlO_2$ was prepared by another 1.5-fold increase of sample size using a custom-made pressure reactor setup (Premex) equipped with a 300 ml PTFE lined Hastelloy C-22 pressure vessel, stirrer and additional top-heating.

The presence of Ag trace amounts (< 1 wt.-%) is evidenced by PXRD analysis for the non-optimized reaction conditions (14h, Scale-Up). Either further parameter adaptation or post-synthesis purification by diluted HNO_3- treatment (5 M, 45 min) are necessary to obtain phase-pure 3R-$AgAlO_2$.

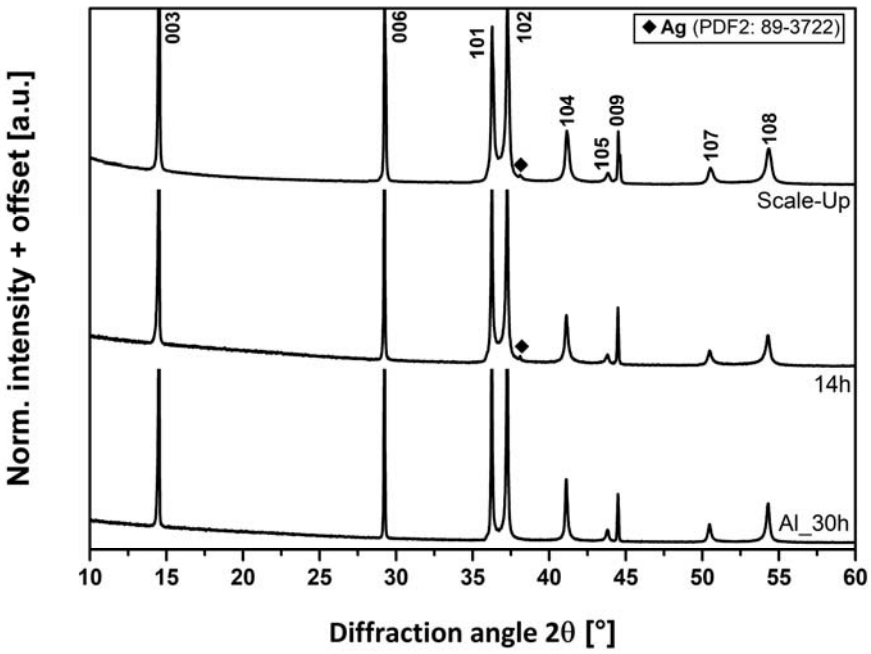

Figure S6: Close ups of PXRD data of Al_30h (3R-$AgAlO_2$), 14h (agitation) and scale-up synthesis. Reflections of 3R-$AgAlO_2$ indexed.

S2.2 3R-$AgGaO_2$

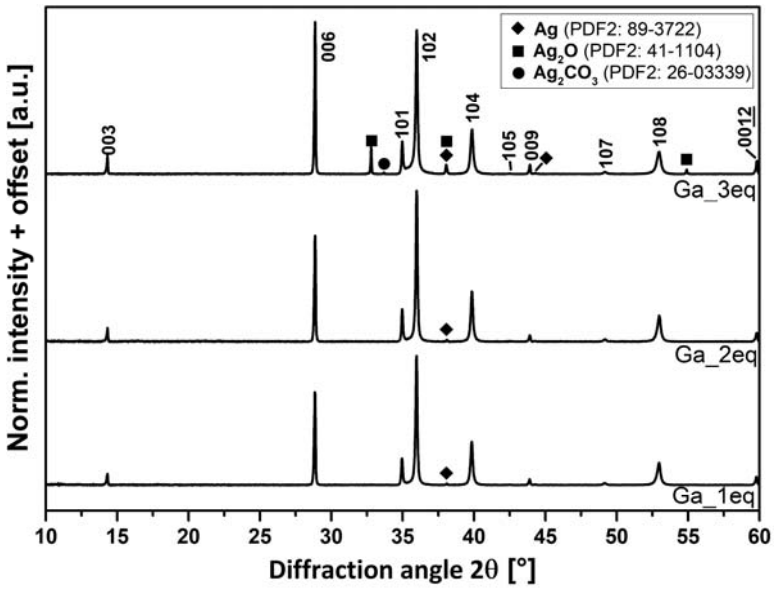

Figure S7: Powder XRD patterns of samples obtained by variation of educt ratios. Reflections of 3R-$AgGaO_2$ indexed.

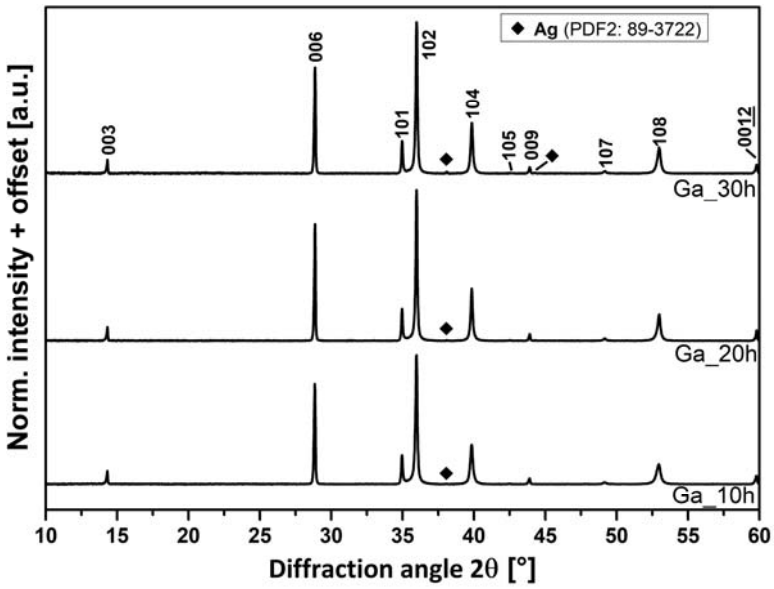

Figure S8: Powder XRD patterns of samples obtained by variation of the hydrothermal synthesis time. Diffraction peaks of 3R-$AgGaO_2$ indexed.

S2.3 3R-$AgInO_2$

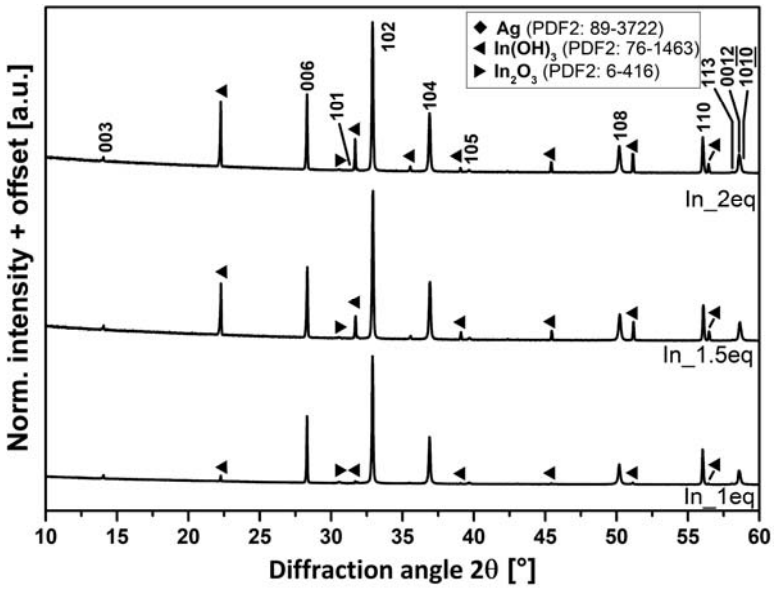

Figure S9: Powder XRD patterns of as-prepared samples obtained by variation of educt ratio. Diffraction peaks of 3R-$AgInO_2$ indexed.

S3 Characterization

S3.1 TEM analysis

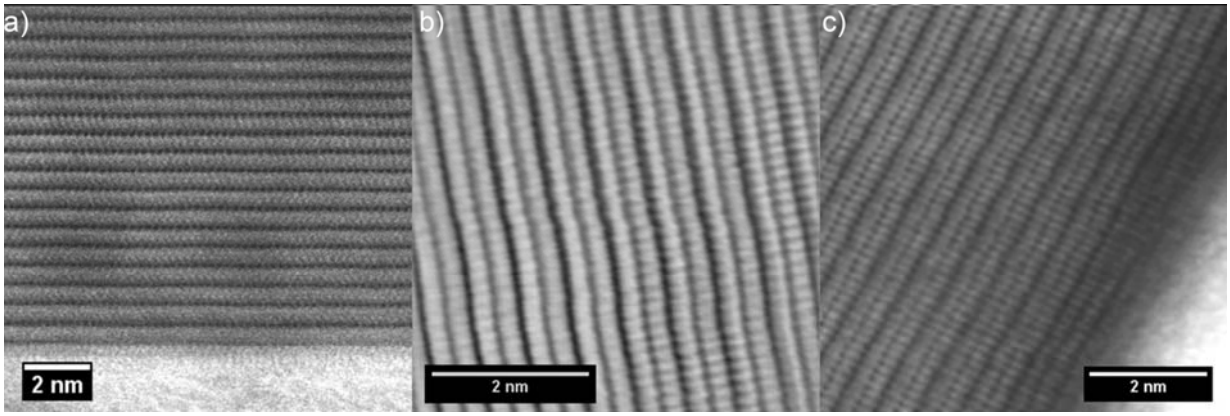

Figure S10: Atomic resolution ABF images of the layered crystalline delafossite structures of a) 3R-$AgAlO_2$ along the [010] zone axis, b) 3R-$AgGaO_2$ along the [120] zone axis and c) 3R-$AgInO_2$ along the [120] zone axis.

S3.2 XPS analysis

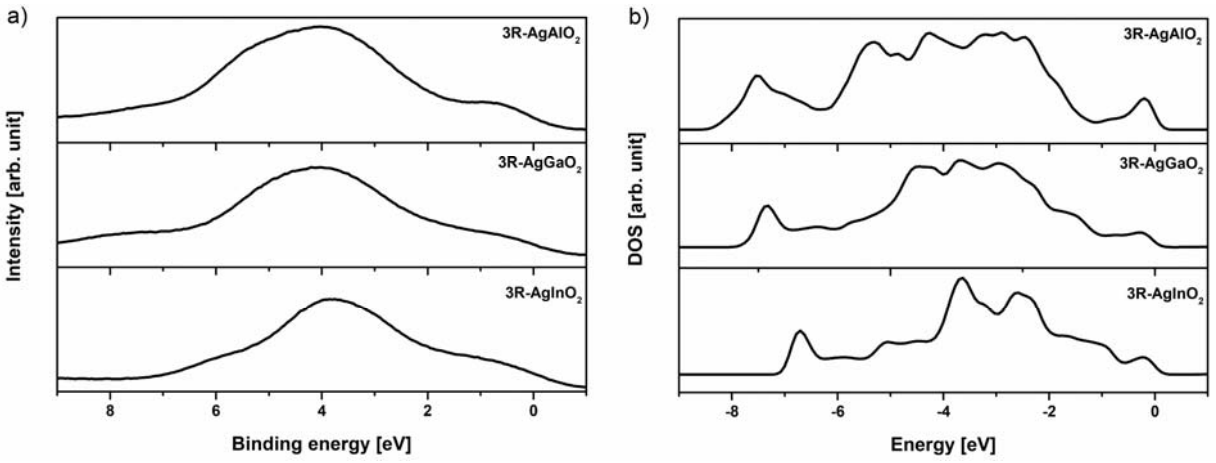

Figure S11: XPS valence band spectra (a) and calculated total DOS (b) of 3R-$AgAlO_2$ (top), 3R-$AgGaO_2$ (middle) and 3R-$AgInO_2$ (bottom panel).

S3.3 DRS

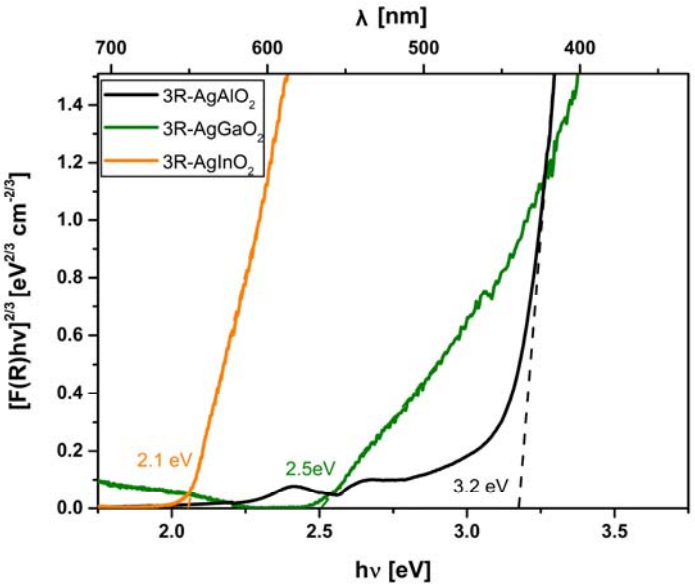

Figure S12: Estimated band gaps from the Tauc plots of 3R-Ag*B*O_2 (*B*: Al, Ga, In).

S3.4 Conductivity

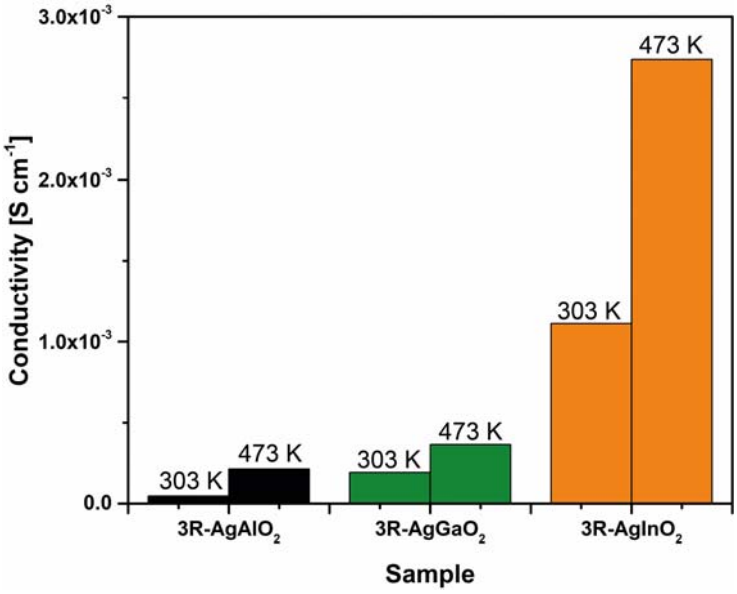

Figure S13: Conductivity of 3R-Ag*B*O_2 (*B*: Al, Ga, In) as a function of temperature.

S3.2 Thermal reactivity of 3R-Ag*B*O_2

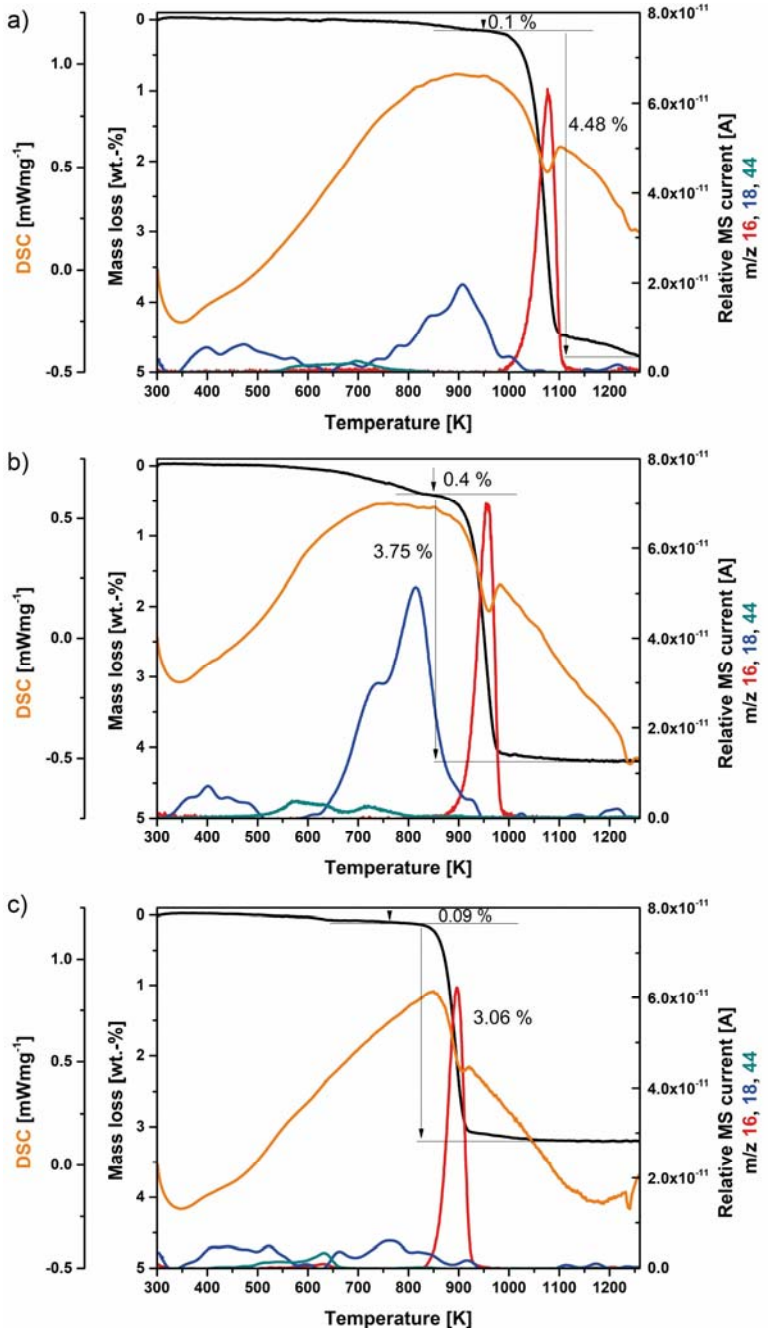

Figure S14: STA/EGA results are given for 3R-$AgAlO_2$ (a), 3R-$AgGaO_2$ (b) and 3R-$AgInO_2$ (c). Mass loss (black line), DSC curve (orange line) and mass spectrometer signal of O (m/z 16, red curve), H_2O (m/ 18, blue curve) and CO_2 (m/z 44, dark cyan curve) are given. STA data (NETZSCH Proteus Thermal Analysis software package, V. 6.10) and EGA data smoothed. The intense O_2 signal (m/z 32) is not shown, due to graphical reason.

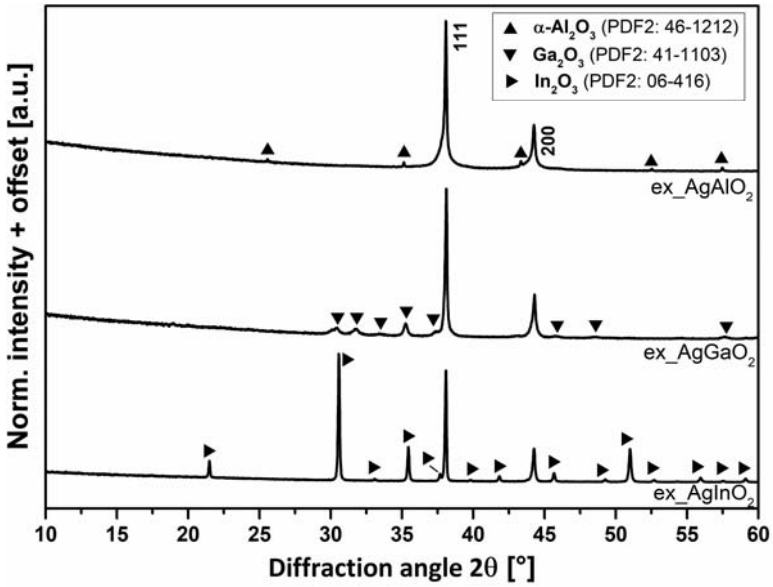

Figure S15: Powder XRD patterns of samples after STA-EGA investigations. Diffraction peaks of Ag (PDF2: 89-3722) indexed.

Temperature-programmed oxidation (TPO) was performed in a fixed-bed quartz reactor using up to 1.5 g 3R-Ag*B*O_2 (*B*: Al, Ga, In). Prior to the experiment, the sample was pre-treated at 873 K (*B*: Al), 823 K (*B*: Ga) or 773 K (*B*: In) for 60 min in He (100 $mlmin^{-1}$, heating rate 5 $Kmin^{-1}$). The selected temperatures ensured the integrity of the samples preventing their unintended decomposition (which would lead to the release of oxygen). The sample was cooled back to 300 K in He (100 $mlmin^{-1}$). The TPO measurement was performed in 0.25 % O_2/He (100 $mlmin^{-1}$), by applying the same heating rate and dwell time as in the pretreatment. During the experiment, the oxygen consumption was monitored with a paramagnetic detector.

TPO results for 3R-$AgAlO_2$ are given in Figure S16. No O_2 uptake could be detected in the experiment.

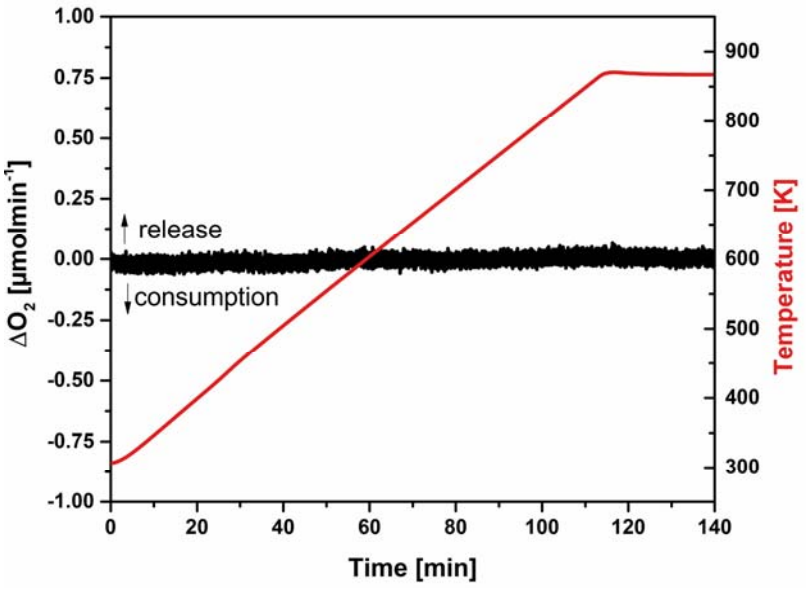

Figure S16: Evolution of the O_2 consumption (-)/evolution (+) rate as a function of the temperature during TPO of 3R-$AgAlO_2$ in 0.25 % O_2/He.