Supporting Information

1. Sol synthesis. For the preparation of a $CuCr_{0.975}Mg_{0.025}O_2$ sol 10.2 g (0.051 mol) copper(II) acetate monohydrate (Fluka, purity ≥99.0%) were dissolved in a mixture of 100 g ethanol (Jäkle, 99.5%) and 26.7 g (0.18 mol) triethanolamine (Fluka, ≥99.0%) by stirring at room temperature for 2 h. To this clear deep blue solution 0.28 g (0.0013 mol) magnesium acetate tetrahydrate (Merck, ≥99.5%) and 12.3 g (0.050 mol) chromium(III) acetate monohydrate (Wako Chemicals, ≥90%) were added and stirring was continued for another 15 h until a clear green liquid had formed. Finally the sol was pressure-filtered through an 0.45 µm nylon filter.

Sols for the preparation of oxides with higher dopant concentrations were prepared in the same manner. Only the masses of the reactants had to be slightly adjusted. For the $CuCr_{0.925}Mg_{0.075}O_2$ sol 10.3 g (0.052 mol) copper(II) acetate monohydrate, 100 g ethanol, 26.9 g (0.18 mol) triethanolamine, 0.83 g (0.0039 mol) magnesium acetate tetrahydrate and 11.8 g (0.048 mol) chromium(III) acetate monohydrate were used. The sol for the oxide stoichiometry $CuCr_{0.900}Mg_{0.100}O_2$ was made up of 10.3 g (0.052 mol) copper(II) acetate monohydrate, 100 g ethanol, 27.1 g (0.18 mol) triethanolamine, 1.11 g (0.0052 mol) magnesium acetate tetrahydrate and 11.5 g (0.047 mol) chromium(III) acetate monohydrate. These masses were altered to 10.4 g (0.052 mol) copper(II) acetate monohydrate, 99.9 g ethanol, 27,2 g (0.18 mol) triethanolamine, 1.40 g (0.0065 mol) magnesium acetate tetrahydrate and 11.3 g (0.046 mol) chromium(III) acetate monohydrate for the $CuCr_{0.875}Mg_{0.125}O_2$ sol. For the preparation of the $CuCr_{0.850}Mg_{0.150}O_2$ sol 10.4 g (0.052 mol) copper(II) acetate monohydrate, 99.8 g ethanol, 27.3 g (0.18 mol) triethanolamine, 1.69 g (0.078 mol) magnesium acetate tetrahydrate and 11.0 g (0.045 mol) chromium(III) acetate monohydrate were weighed in.

2. Thermogravimetry and differential thermal analysis. Figure S1 shows the according analysis results of an ethanol-based dried $CuCrO_2$ sol in synthetic air. Up to a temperature of 200 °C the weight loss remains below 3%, which can be interpreted as a loss of some stubborn solvent molecules and traces of water. At higher temperatures a strongly exothermic reaction sequence is initialized and seems to be completed at about 400 °C. More than 69% of the sample weight are lost during this sequence. Obviously the organic complexing agents and anions are burnt, leaving behind pure metal oxide (cp. XRD data, Figure 1). A last reaction step becomes apparent at about 850 °C and lasts until 900 °C. The DTA shows a slightly exothermic bow in this range. Hence it might be correlated to the transformation of CuO and the spinel phase into delafossite, driven by entropy.

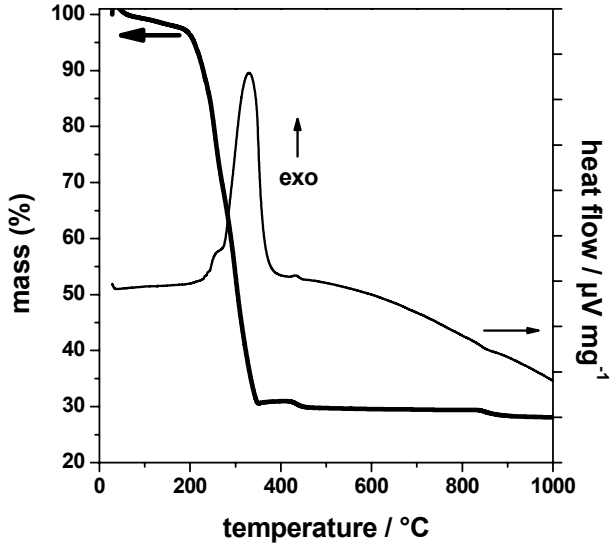

Figure S1: *Results of the thermogravimetry (TG, left axis) and differential thermal analysis (DTA, right axis) of a dried $CuCrO_2$ sol in synthetic air. The heating rate was 10 K/min.*

3. Tauc Plot data. *Figure S2 shows the Tauc-plot of the indirect bandgap of $Cu(Al_{0.5}Cr_{0.5})O_2$, while Figure S3 and S4 present the respective plots for 2.5% and 10% magnesium doping. Figure S5 displays the Tauc plot of the undoped $CuCrO_2$ system.*

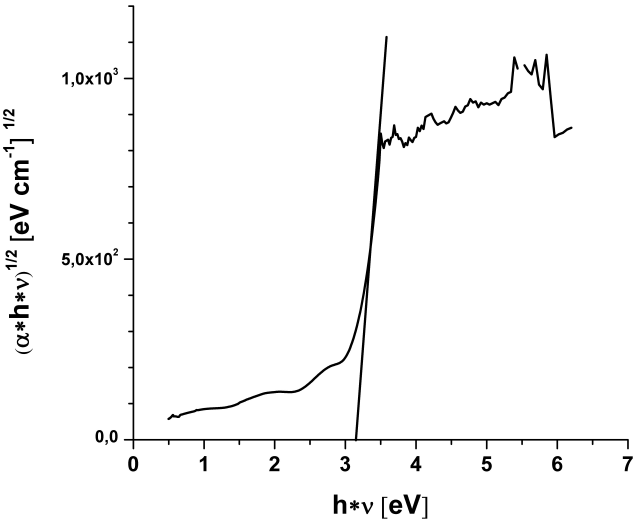

Figure S2: Tauc plot of the $Cu(Al_{0.5}Cr_{0.5})O_2$ system sintered at 750 °C.

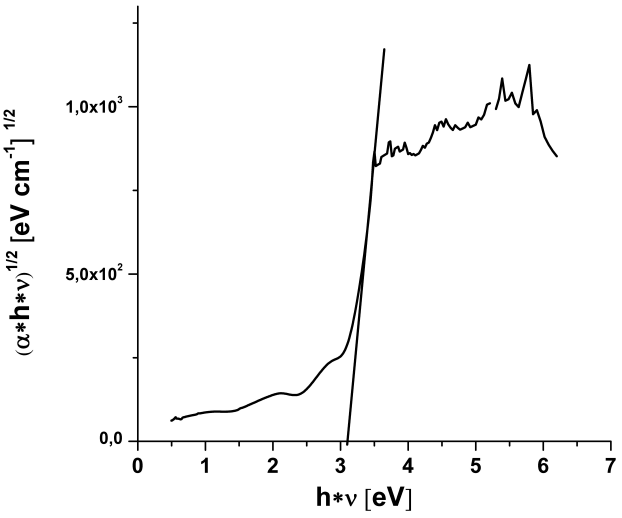

Figure S3: Tauc plot of the $Cu(Al_{0.4875}Cr_{0.4875}Mg_{0.025})O_2$ system sintered at 750 °C.

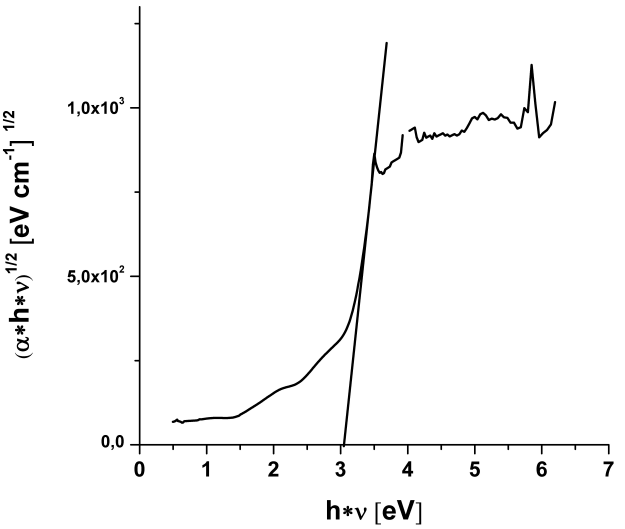

Figure S4: Tauc plot of the $Cu(Al_{0.45}Cr_{0.45}Mg_{0.1})O_2$ system sintered at 750 °C.

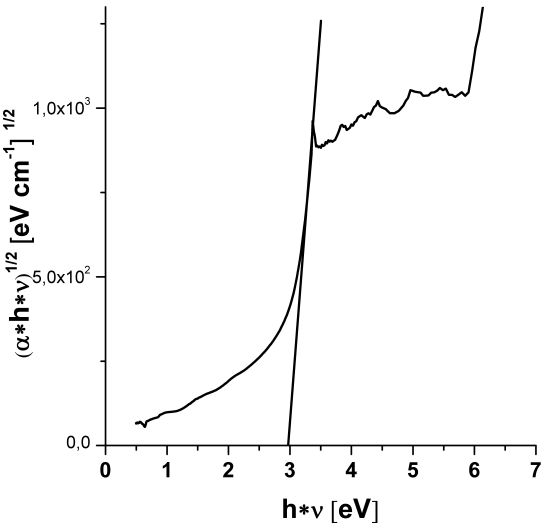

Figure S5: Tauc plot of the undoped $CuCrO_2$ system sintered at 750 °C.