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Photocatalytic CO₂ Reduction by Cr-substituted

Ba₂(In_{2-x}Cr_x)O₅·(H₂O)_δ (0.04 ≤ x ≤ 0.60)

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Abstract

Cr-substituted polycrystalline Ba₂(In_{2-x}Cr_x)O₅·(H₂O)_δ powders (0.04 ≤ x ≤ 0.60) were synthesized by solid state reaction to investigate the relation of crystal structure, thermochemical, magnetic, and optical properties. The Cr-substitution results in an unit cell expansion and formation of the higher-symmetric tetragonal phase together with increased oxygen and hydrogen contents. Magnetic property measurements reveal that the diamagnetic pristine Ba₂In₂O₅·(H₂O)_δ becomes magnetically ordered upon Cr-substitution. By UV–vis spectroscopy a gradual shift of the absorption-edge energy to lower values was observed. Numerical calculations showed that the observed bandgap narrowing was ascribed to the Cr induced states near the Fermi level. The correlation between the changes of crystal chemistry, magnetic, and optical properties of Cr-substituted Ba₂(In_{2-x}Cr_x)O₅·(H₂O)_δ can be explained by the replacement of In by Cr. Consequently, an enhanced photocatalytic CO₂ reduction activity was observed with increasing Cr substitution, compatible with the state-of-the-art high surface area TiO₂ photocatalyst (P-25).

Keywords: Photocatalytic CO₂ reduction, Ba₂In₂O₅, DFT, Cr-substitution, Le Bail fit, crystal chemistry, magnetic property, optical property

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I. Introduction

$\text{Ba}_2\text{In}_2\text{O}_5$ has a brownmillerite structure (oxygen-deficient perovskite-related structure), which can be described as a stacking of alternating layers of InO_4 tetrahedra and InO_6 octahedra with Ba^{2+} ions. $\text{Ba}_2\text{In}_2\text{O}_5$ has drawn increasing research interest regarding fast oxide ion and proton conduction due to its unique crystal structure [1–6]. Partial cationic and/or anionic substitution in $\text{Ba}_2\text{In}_2\text{O}_5$ brings marked changes in crystal structure, defect structure, and electronic structure resulting in a number of materials properties, which are interesting for various technical applications [2,7–19]. For example, gallium or zirconium substituted $\text{Ba}_2\text{In}_2\text{O}_5$ for solid oxide fuel cells (SOFC) with an intermediate operating temperature range of 823 – 1023 K was a research focus in recent years [13,20–22]. Lately, the magnetic properties of Ir-, Mn-, and Co-substituted $\text{Ba}_2\text{In}_2\text{O}_5$ were investigated [7,23,24]. Flynn *et al.* inferred a large spin–orbit coupling from the magnetization of the Ir-containing solid solution $\text{Ba}_2\text{In}_{2-x}\text{Ir}_x\text{O}_{5+\delta}$ [7]. Jiang *et al.* reported that for all values of x the Mn ions in $\text{Ba}_2\text{In}_{2-x}\text{Mn}_x\text{O}_{5+x}$ ($x = 0.1\text{--}0.7$) predominantly occur as Mn^{5+} with paramagnetic spin-only moments [23]. Interestingly, spin glass behavior was confirmed for Co-substituted $\text{Ba}_2\text{In}_{2-x}\text{Co}_x\text{O}_5$ ($x = 0.70, 1, 1.70$) [24]. On the other hand, the influence of hydration/dehydration on the crystal chemistry of $\text{Ba}_2\text{In}_2\text{O}_5 \cdot (\text{H}_2\text{O})_\delta$ has been studied more out of a fundamental interest [25–30].

In our previous study, we have shown that the crystal structure, optical, and magnetic properties can be substantially altered by the replacement of tetrahedral InO_4 units by octahedral CrO_6 units in $\text{Ba}_2(\text{In}_{1.8}\text{Cr}_{0.2})\text{O}_5 \cdot (\text{H}_2\text{O})_\delta$ [31]. The magnetic properties of Cr-substituted $\text{Ba}_2\text{In}_2\text{O}_5$ have not been studied in detail. Moreover, no systematic investigation on the Cr substitution effect on the crystal structure, the oxygen content and degree of hydration, and optical properties has been carried out. In this study, $\text{Ba}_2(\text{In}_{2-x}\text{Cr}_x)\text{O}_5 \cdot (\text{H}_2\text{O})_\delta$ with different Cr contents was synthesized via solid state reactions. The changes in long- and short-range ordering of the crystal structure were investigated by powder X-ray diffraction (XRD) and Raman spectroscopy. Elemental analysis and thermal gravimetric analysis (TGA) were conducted to elucidate the nature of chemical bonding. As far as we know, photocatalytic CO_2 reduction together with theoretical studies on pristine and Cr-substituted $\text{Ba}_2\text{In}_2\text{O}_5$ has not been reported. In the present study, we report the photocatalytic CO_2 -reduction activity of Cr-substituted $\text{Ba}_2(\text{In}_{2-x}\text{Cr}_x)\text{O}_5 \cdot (\text{H}_2\text{O})_\delta$ powders. Finally, the correlation between the photocatalytic activity and bandgap changes of Cr-substituted $\text{Ba}_2\text{In}_2\text{O}_5 \cdot (\text{H}_2\text{O})_x$ is discussed.

II. Experimental Procedures

A series of polycrystalline $\text{Ba}_2(\text{In}_{2-x}\text{Cr}_x)\text{O}_5 \cdot (\text{H}_2\text{O})_\delta$ ($x = 0.04, 0.08, 0.12, 0.16, 0.40$, and 0.60) powders was synthesized by solid state reactions. As-synthesized powders are hereinafter referred to Cr04, Cr08, Cr12, Cr16, Cr40, and Cr60, respectively. Appropriate amounts of BaCO_3 (Merck, ACS 99%), In_2O_3 (Alfa Aesar, 99.9%), and Cr_2O_3 (Alfa Aesar, 99.97%) powders were thoroughly mixed using an agate mortar and pestle, and calcined in air at 1123 K for 12 h, then at 1373 K for 12 h, and finally at 1573 K for 12 h with intermittent grinding steps. The applied heating and cooling rate was 5 K/min, respectively. As-prepared powders were treated and stored in ambient air conditions unless otherwise indicated. The oxygen and hydrogen contents of the product powders were determined by the hot-gas extraction method using a ELTRA ONH 2000 analyzer. To determine the oxygen contents, about 5–10 mg sample was placed in a Sn (99.9%) crucible with 100 mg Ni flux and rapidly heated to about 3300 K under He (99.999%) atmosphere using an electrode impulse furnace. Hydrogen was detected under N_2 (99.999%) atmosphere. The measurements were repeated three times for each sample and the obtained oxygen and hydrogen amounts were averaged.

To characterize the specific surface area, nitrogen adsorption and desorption isotherms at 77 K were performed using an Autosorb-3B manufactured by Quantachrome. Data analysis was accomplished using the *ASiQwin* software (ver. 3.01). Prior to the experiments, the catalysts were pretreated under vacuum at 623 K for 16 h. The total surface area of the catalysts was evaluated by the Brunauer–Emmett–Teller (BET) method within the linear relative pressure range ($p/p_0 = 0.01$ to 0.3).

Powder X-ray diffraction (XRD) patterns were obtained using a Rigaku Smartlab θ - θ scan system ($\text{Cu-K}_{\alpha 1,2}$ radiation) equipped with a thin Ni foil as Cu-K_β filter (approximately 90% efficiency). The diffraction patterns were recorded in a 2θ range of 10° to 140° with an angular step interval of 0.02° at room temperature. XRD patterns were analyzed with the Le Bail method incorporated in the Rietveld refinement program *Fullprof* to determine the unit cell parameters. The Thompson-Cox-Hastings pseudo-Voigt function was chosen as a profile function.

Raman spectra were recorded at room temperature using a Kaiser Optical Holospec monochromator equipped with a liquid nitrogen cooled CCD camera. A He-Ne laser with 50 mW power at an excitation wavelength of 632.8 nm was utilized with a cylindrical lens on the sample.

The powdered samples were contained in glass melting point capillary tubes. Additional Raman spectra were obtained with a Renishaw InVia Raman microscope using 632.8 nm excitations.

Thermal gravimetric analysis (TGA) was carried out by using a NETZSCH STA 449C Jupiter thermobalance coupled to an InProcess Instruments GAM 200 mass spectrometer. Around 100 mg powder sample was heated in an alumina crucible in Ar (99.999%, 150 mL/min) at a heating rate of 10 K/min from room temperature to 1573 K.

DC magnetic properties of the samples were determined by means of a superconducting quantum interference device (SQUID). The temperature dependent susceptibility was measured in the temperature range of 2 – 300 K at 0.5 T. The field dependent measurements were conducted in the external field range of 7 T to –7 T at both 1.8 K and room temperature.

UV-visible diffuse reflectance spectra were obtained using a Shimadzu UV–3600 UV–VIS NIR spectrophotometer equipped with an integrating sphere. The baseline was measured with BaSO₄. Spectra were recorded in the range of 200 to 800 nm. The Kubelka-Munk conversion was applied to the obtained reflectance spectra and the bandgap wavelength was estimated by extrapolating the onset of absorption to the wavelength axis.

For our first principles calculations density functional theory is used as implemented in the Vienna Ab-initio Simulation Package [32]. A kinetic energy cutoff of 500 eV and the generalized gradient approximation of Perdew, Burke, and Ernzerhof to the exchange–correlation functional are used. We build a Ba₈In₈O₂₀ supercell (total 36 atoms) using space group *Ibm2* (see Fig. 6) as employed in previous theoretical studies [5,33]. Using a $5 \times 2 \times 5$ *k*-mesh (Monkhorst-Pack scheme), the model structures are fully relaxed until the total energy change is within 10^{–6} eV and the atomic forces are converged within 0.01 eV/Å. An on-site Coulomb energy of 3 eV is taken into account for modeling the electron-electron correlation effects of the localized Cr 3*d* orbitals [34].

The photocatalytic activity was investigated in a fixed bed photoreactor made of stainless steel. The reactor was equipped with a fused silica window. A water-cooled medium pressure mercury lamp (TQ-150, Peschl Ultraviolet GmbH, Mainz, Germany) was used for irradiation and installed close to the reactor window. The reactor was tempered to room temperature. CO₂ and H₂ were fed into the reactor by use of mass flow controllers (Bronckhorst High-Tech B.V. Ruurlo, The Netherlands) calibrated to the respective gases. The flow chart is given in Supporting information S1. The gases leaving the reactor were analyzed with an online gas chromatograph. For this, an Agilent 7890A gas chromatograph equipped with a HP5 (5%-phenyl)-

methylpolysiloxane capillary column and a ShinCarbon ST80/100 column was used. A volume of 500 μL was injected through a sample loop. The initial oven temperature was set to 305 K. After 3 min the temperature was raised to 473 K with a heating rate of 15 K/min. The catalyst (ca. 0.3 g) was evenly distributed in a dedicated well. Experiments were conducted with flow rates of 6.52 mL min^{-1} for CO_2 and H_2 . The light source was switched on 15 min before the first experiment was started to ensure a constant light output. *Measurements of the photocatalytic activity were repeated every 15 minutes with 3 minute of pause between the measurements during continuous irradiation, and the obtained conversion rate was averaged.* Reference data required to calculate the conversion were gathered with experiments, for which the reactants were guided through a bypass line to avoid any reaction.

III. Results

Figure 1 shows the powder X-ray diffraction patterns of the synthesized Cr04, Cr08, Cr12, Cr16, Cr40, and Cr60 samples. Except for Cr60, all observed reflections were indexed to an orthorhombic brownmillerite structure (space group: *Icmm*) [3,13] providing the absence of any remaining precursors or impurity phases. A small quantity of secondary phase was only found in the Cr60 sample and identified as BaCrO_4 (JCPDS No. 00-035-0642). With increasing Cr-substitution, a drastic intensity decrease of the (020) reflection at 10.4° in 2θ was observed. The shifts and changes of other reflections are shown and discussed in the Supporting information S2. The lattice parameters derived from Le Bail fitting results are listed in Table 1 and a representative fitting plot for Cr40 is presented in Figure S3 in the Supporting information.

For Cr04, Cr08, Cr12, and Cr16, the lattice parameter a decrease, while in reverse lattice parameters b and c increase, resulting in an increased unit cell volume with ascending Cr substitution. The unit cell parameters of Cr40 and Cr60 are only subtly different from Cr16. The difference between parameters a and c of all samples decreases with increasing Cr content, potentially indicating a phase-transition to a higher-symmetry tetragonal phase with *I4cm* space group (No. 108) [3].

Figure 2 exhibits the Raman spectra of the six powder samples. With increasing Cr substitution, the most intense, characteristic band at 600 cm^{-1} , which is the typical stretching vibration of In–O bonds in the brownmillerite-type structure [26,35,36], significantly decreased and a new band at 852 cm^{-1} , due to be the vibration of In–O bonds in a perovskite-type structure (absent in pristine $\text{Ba}_2\text{In}_2\text{O}_5 \cdot (\text{H}_2\text{O})_\delta$), became more and more apparent. Other Raman bands of the

Cr-containing samples at e.g., 278, 316, and 526 cm^{-1} were only marginally different from values reported for brownmillerite-type structures [15,35] mostly due to a different oxygen content and degree of hydration, respectively. The low frequency Raman spectra of samples (Cr04, Cr12, Cr16, and Cr40) was measured additionally and shown in the Supporting information S4. While sample Cr04 still presents the sharp bands observed for pristine $\text{Ba}_2\text{In}_2\text{O}_5 \cdot (\text{H}_2\text{O})_\delta$, those sharp bands have disappeared for the samples with higher Cr content. These findings indicate that with Cr substitution the crystal structure changes from brownmillerite-type to perovskite-type by filling of oxygen vacancies from the coordination-unsaturated InO_4 units to the CrO_6 units [36]. Interestingly, an introduction of only 4 mol. % Cr induces an exceptionally intense band at 852 cm^{-1} . One possible explanation is a resonant Raman effect, which occurs when the excitation wavelength of the laser is close or equal to an electronic absorption of the chromophore involving a huge increase in intensity, in particular of bands related to totally symmetrical vibrations [37]. It should also be noted that bands at 526 cm^{-1} are broader and shifts to higher wavenumber with increasing Cr substitution. A shift towards higher frequency can be observed when a larger In^{3+} ion is replaced by a smaller Cr^{3+} ion [38]. Thus, the Raman spectra reveal a gradual structural change of Cr-substituted barium indate from the brownmillerite-type to the perovskite-type together with the formation of a secondary phase at highest substitution content.

Figure 3 displays the results of TGA-MS analyses. Figure 3(a) shows the mass changes of the six powder samples during heating in Ar. A mass loss was observed for all samples (Table 2), which up to the Cr16 sample was the more pronounced the higher Cr content. Cr40 and Cr60 slightly differed from the other four samples. The peaks of the differential thermal gravimetry (DTG) profiles (Fig. 3(b)) are located at approximately 600 K for Cr04, Cr08, Cr12, and Cr16, and at 500 K for Cr40 and Cr60. The gases evolved during the mass changes were analysed by mass spectrometry. The MS-signal of H_2O ($m/z = 18$) and CO_2 ($m/z = 44$) are plotted in Fig. 3(c) and (d). For all samples, the maximum peak of the H_2O MS-signal corresponds well with the DTG signal clearly indicating that the mass losses are associated with H_2O release from $\text{Ba}_2(\text{In}_{2-x}\text{Cr}_x)\text{O}_5 \cdot (\text{H}_2\text{O})_\delta$ [16,25,30]. The higher the Cr content, the more H_2O is found to be incorporated in the structure. This trend is consistent with the elemental analysis listed in Table 2. The origin of the minor peak at 915 K (marked as *) in Fig. 3(c), which is only observed for Cr12 and Cr16, remains yet unclear. Even though the MS-signal intensity of CO_2 was one order of magnitude lower than that of H_2O , separated peaks can be attributed to the release of CO_2 in the temperature range of 900 K < T < 1400 K.

The magnetization M of the six powder samples was measured. The temperature dependent susceptibility χ (M - T curves) and the field dependent magnetization at 1.8 K (M - H curves) are shown in Fig. 4(a) and (b), respectively. A common feature of both the M - T and the M - H curves is that the six samples can be divided into two groups regarding their magnetic properties. The susceptibility data of the four samples Cr04, Cr08, Cr12, and Cr16 indicate the transition from effective diamagnetic behavior (negative susceptibility) to magnetic ordering with decreasing temperature due to the presence of magnetic Cr ions (Fig. 4(a)). In contrast, samples Cr40 and Cr60 show positive susceptibility in the whole temperature range (inset of Fig. 4(a)). At elevated temperatures in the paramagnetic range of Cr^{3+} ions ($80 \text{ K} < T < 300 \text{ K}$), the susceptibility (χ) can be fitted with a modified Curie-Weiss law

$$\chi = \frac{C}{T - \theta} + \chi_0 \quad (1)$$

where χ_0 is the temperature independent susceptibility of diamagnetism from pristine $\text{Ba}_2\text{In}_2\text{O}_5 \cdot (\text{H}_2\text{O})_8$, C the Curie constant, and θ the Weiss temperature, which is known as Curie temperature (T_C) or Neel temperature (T_N) for ferromagnetic and antiferromagnetic compounds, respectively. The fitting results of the susceptibility curves in the paramagnetic range of the Cr^{3+} ion are presented in Table 3. C , θ and T_C show a systematical variation with increasing Cr content. The Weiss constant θ results support the magnetic configuration. While an antiferromagnetic structure of the Cr04, Cr08, Cr12, and Cr16 samples can be deduced from the negative value of θ , the positive θ of the Cr40 and Cr60 samples indicate ferromagnetic behavior. M - H curves of Cr04, Cr08, Cr12, and Cr16 at 1.8 K (Fig. 4(b)) and room temperature (Supporting information S5) clearly differ from those of Cr40 and Cr60. At room temperature, Cr04, Cr08, Cr12, and Cr16 are diamagnetic, whereas Cr40 and Cr60 show paramagnetic behavior. This difference can be explained by the concept of magnetic Cr ions dispersed in a diamagnetic $\text{Ba}_2\text{In}_2\text{O}_5 \cdot (\text{H}_2\text{O})_8$ surrounding for Cr04, Cr08, Cr12, and Cr16, while the paramagnetic behavior of Cr40 and Cr60 is related to the strong interaction of Cr^{3+} ions, whose distance become shorter with increasing Cr substitution.

Figure 5 shows the UV-visible diffuse reflectance spectra as a function of the wavelength. A systematic variation in the absorption edge with Cr-content was observed. The six samples can be divided into two groups in good agreement with the findings of our thermochemical and

magnetic studies. For the four samples Cr04, Cr08, Cr12, and Cr16 the absorption edge wavelength was shifted gradually to a higher values with increasing Cr substitution, rising from approximately 600 nm (bandgap $E_g = 2.07$ eV) to about 628, 653, and 678 nm ($E_g = 1.97$, 1.90, and 1.83 eV), respectively. This bandgap narrowing effect was ascribed to electronic bands formed by Cr [39]. Further Cr substitution in $\text{Ba}_2\text{In}_2\text{O}_5 \cdot (\text{H}_2\text{O})_6$ leads to absorption at even longer wavelength and the estimated bandgap E_g of Cr40 and Cr60 was 1.15 and 1.25 eV, respectively. As shown in Fig. 4, the color of the powders changed from light orange (Cr04) to dark red (Cr16) and dark brown (Cr40 and Cr60).

In order to theoretically investigate the effect of Cr substitution on the electronic band structure of $\text{Ba}_2\text{In}_2\text{O}_5$, we substitute one In atom by a Cr atom, which corresponds to 12.5 % substitution. Fig. 6(a) shows that in pristine $\text{Ba}_2\text{In}_2\text{O}_5$ (space group: *Ibm2*) the In atoms occupy two crystallographic sites. On the first site each In atom is surrounded by four O atoms in tetrahedral coordination geometry, while on the second site each In atom is surrounded by six O atoms, in octahedral coordination geometry. Energetic analysis shows that Cr substitution at the octahedral site has a lower energy than at the tetrahedral site. For pristine $\text{Ba}_2\text{In}_2\text{O}_5$ a band gap of 0.96 eV (direct) is obtained, which reduces to 0.46 eV (indirect) upon 12.5% Cr substitution. This reduction in bandgap is in agreement with the experimental results. We note that the theoretical bandgap values are lower than the experimental values, which is a well-known underestimation and does not affect the prediction of trends [40–42]. Figs. 6(a) and (b) show the electronic band structure and corresponding density of states for pristine and 12.5 % Cr-substituted $\text{Ba}_2\text{In}_2\text{O}_5$, respectively. The reduction in band gap upon Cr substitution is found to be due to the appearance of Cr states near the Fermi level.

Finally, photocatalytic activity for CO_2 reduction of various Cr-substituted $\text{Ba}_2(\text{In}_{2-x}\text{Cr}_x)\text{O}_5 \cdot (\text{H}_2\text{O})_6$ catalysts is shown in Figure 7. The activity increases with the Cr content from a conversion per mass of 0.8×10^{-4} /mg for $x = 0.02$ to 4.56×10^{-4} /mg for Cr60. The observed activity for Cr60 is nearly the same as for P-25 within the estimated error range, which was used as a benchmark catalyst. It should be mentioned here that the BET surface area of the Cr60 sample was only 0.191 m^2/g , while that of P-25 was around 35–65 m^2/g . Therefore, it can be concluded that Cr-substituted $\text{Ba}_2(\text{In}_{2-x}\text{Cr}_x)\text{O}_5 \cdot (\text{H}_2\text{O})_6$ catalysts showed much better photocatalytic activity than P-25 when it is normalized to the available surface area.

IV. Discussion

Figure 8 shows master curves of selected experimental data as a function of the Cr content. Based on our results, we can divide the samples in two groups. One group, comprising the samples Cr04, Cr08, Cr12, and Cr16, features systematic changes in terms of crystal chemistry, magnetic, and optical properties. The other group, comprising the samples Cr40 and Cr60, shows strong contributions of a secondary phase to the material properties. This result confirms the conclusion from our previous study [31], the replacement of tetrahedral InO_4 units by octahedral CrO_6 units leads to drastic changes in crystal structure, magnetic, and optical properties. The substitution of Cr^{3+} for In^{3+} enlarges the unit cell and strengthens the stability of the higher-symmetry tetragonal phase together with increased oxygen and hydrogen contents, which can be explained by the substitution of octahedral CrO_6 for tetrahedral InO_4 units. As a result, the spin-spin interaction changes and the bandgap is narrowed accordingly by the new band formation in the middle of the bandgap. The final heat treatment of the Cr-substituted and the pristine samples conducted at 1573 K for 12 h led to a different crystal structure and composition (oxygen and hydrogen content), in contrast to 1473 K for 12 h, which rules out their direct comparison regarding the origin of magnetic and optical properties changes.

It was shown that the refinements of XRD patterns with both *Icmm* and *Ibm2* space groups resulted in acceptable χ^2 values in our previous study [31]. The only difference between these two space groups is the degree of orientational correlation and disorder between adjacent layers of InO_4 tetrahedra. Therefore, the choice of *Ibm2* instead of *Icmm* in DFT calculation would not be a critical factor that can cause the drastic change in calculated total density of states. Besides, it should be noted that Cr substitution is energetically favorable at the octahedral site as compared to the tetrahedral site according to our first principle calculations, which contradicts our previous experimental study on the site occupation of Cr [31]. Based on the similarity of ionic radii of octahedral Cr^{3+} ($r(\text{Cr}^{3+})_{\text{VI}} = 0.615 \text{ \AA}$) and tetrahedral In^{3+} ($r(\text{In}^{3+})_{\text{IV}} = 0.620 \text{ \AA}$) [43], it is proposed that replacement of tetrahedral InO_4 units by octahedral CrO_6 units is favored in $\text{Ba}_2(\text{In}_{1.8}\text{Cr}_{0.2})\text{O}_5 \cdot (\text{H}_2\text{O})_\delta$. This conclusion was also supported by the increased unit-cell volume as well as the oxygen and hydrogen contents. It must be emphasized that in our calculations the influence of existing water (hydroxyl ions) was not considered, which may play a certain role in the relaxation of our model structures. This discrepancy between theory and experiment remains an open question.

It is well known that the crystal structure of $\text{Ba}_2\text{In}_2\text{O}_5$ provides channels easily accessible for H_2O molecules leading for instance to the hydrated phase BaInO_3H [28]. Bielecki et al. [26] investigated systematically the influence of hydration on the short-range structure of $\text{Ba}_2\text{In}_2\text{O}_5$. The Raman spectra in Ref. 26 clearly showed a distinctive difference in the distinguishable band positions with and without hydration. In this study, however, with increasing Cr substitution the pronounced Raman band starts to be reduced significantly in intensity. By elemental analysis and TGA (Table 2), we found that the H_2O contents in $\text{Ba}_2\text{In}_2\text{O}_5$ increased with increasing Cr substitution, but according to our XRD data it seems that H_2O molecules do not incorporate in an ordered form. Instead a random orientation might be preferred. Further studies are currently underway by using FT-IR and low wavenumber high resolution Raman spectrometry to address this issue.

The increase in photocatalytic activity is attributed to the broadening of the absorption spectra (Figure 5), leading to an increased fraction of absorbed light emitted by the mercury vapor lamp. Conversion is significantly increased by 100 % when the Cr content is raised from $x = 0.04$ to $x = 0.08$. The effect levels off for higher Cr contents, e.g., when x is increased from 0.40 to 0.60 the conversion increases by 50 %. This is a result of the overlap between the absorption spectrum of the material with the emission spectrum of the used light source. The utilized medium pressure mercury vapor lamp emits only up to a wavelength of 578 nm. Hence, a material absorbing at longer wavelengths has no additional effect on the fraction of photons absorbed. Increasing the Cr content increases the number of absorbed photons and results in enhanced photoactivity. This effect becomes less pronounced when the fraction of absorbed photons is already large, which is the case for materials with large Cr contents.

V. Summary

$\text{Ba}_2(\text{In}_{2-x}\text{Cr}_x)\text{O}_5 \cdot (\text{H}_2\text{O})_\delta$ powders ($0.04 \leq x \leq 0.60$) were synthesized by solid state reactions. All samples were characterized structurally as well as chemically, and the associated magnetic and optical properties were studied. The replacement of tetrahedral InO_4 units by octahedral CrO_6 units was found experimentally to be the main factor influencing the magnetic and optical properties. This applies especially to the optical bandgap, which was gradually reduced from 2.07 eV to 1.83 eV with increasing Cr content. We revealed a strong correlation between the crystal chemistry and the magnetic and optical properties of Cr-substituted $\text{Ba}_2(\text{In}_{2-x}\text{Cr}_x)\text{O}_5 \cdot (\text{H}_2\text{O})_\delta$. First

principles calculations on pristine and Cr-substituted models show a reduction in bandgap upon Cr substitution due to the appearance of Cr states near the Fermi level. The photocatalytic CO₂ reduction activity increases with the Cr content, corresponding to the changing optical properties. Ba₂(In_{1.4}Cr_{0.6})O₅·(H₂O)_δ shows an activity similar to that of P-25 even though the active surface area detected by BET is by a factor of about 250 lower.

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Table and Figure Captions

Table 1. Songhak Yoon *et al.*

Table 1. Le Bail fitting results of Cr-substituted $\text{Ba}_2(\text{In}_{2-x}\text{Cr}_x)\text{O}_5 \cdot (\text{H}_2\text{O})_\delta$.

Sample	Unit cell parameter (Å)			Volume (Å ³)	R_p (%)	R_{wp} (%)	R_{exp} (%)	χ^2
	a	b	c					
Cr04	6.0500(3)	16.8202(9)	5.9629(2)	606.80(5)	10.4	14.8	12.25	1.45
Cr08	6.0332(2)	16.8396(6)	5.9753(3)	607.08(4)	11.4	17.1	11.53	2.20
Cr12	6.0379(2)	16.8927(9)	5.9738(3)	609.31(5)	13.5	18.6	13.44	1.93
Cr16	6.0223(2)	16.9169(4)	5.9817(2)	609.40(3)	12.8	18.0	13.55	1.76
Cr40	6.0236(1)	16.9157(3)	5.9813(1)	609.45(2)	12.2	16.9	13.48	1.58
Cr60	6.0272(4)	16.9128(6)	5.9769(2)	609.28(5)	11.6	17.0	12.48	1.86

Space group symmetry: *Icmm*

R_p , R_{wp} , R_{exp} , and χ^2 are the reliability factors and goodness-of-fit, respectively.

The numbers in parentheses are the estimated standard deviations.

Table 2. Songhak Yoon *et al.*

Table 2. Elemental analysis for oxygen and hydrogen together with the mass change observed by TGA of the synthesized samples.

Sample	Oxygen (wt. %)	Hydrogen (wt. %)	Mass change (%) ^a
Cr04	13.8(2)	0.024(1)	0.52
Cr08	13.9(2)	0.025(1)	0.91
Cr12	14.3(2)	0.058(2)	1.47
Cr16	14.5(2)	0.057(2)	1.65
Cr40	14.7(2)	0.056(2)	1.64
Cr60	14.9(2)	0.079(2)	2.55

^a Mass change in the TGA curves was calculated in the temperature range of $400\text{ K} < T < 1500\text{ K}$. The numbers in parentheses are the estimated error of the measurements.

Table 3. Songhak Yoon *et al.*

Table 3. The fitting parameters of the Curie-Weiss analysis of Cr-substituted $\text{Ba}_2(\text{In}_{2-x}\text{Cr}_x)\text{O}_5 \cdot (\text{H}_2\text{O})_y$; C is the Curie constant, θ the Weiss temperature, χ_0 the temperature independent contribution.

Sample	Curie constant, C (emu·K/g·Oe)	Weiss temperature, θ (K)	χ_0 (emu/g·Oe)
Cr04	0.00293(2)	-85(9)	-1.46×10^{-4}
Cr08	0.00318(8)	-18(2)	-1.41×10^{-4}
Cr12	0.00336(7)	-2(1)	-1.37×10^{-4}
Cr16	0.00440(1)	-0.2(2)	-1.39×10^{-4}
Cr40	0.0424(2)	3.4(3)	-0.81×10^{-4}
Cr60	0.0487(3)	2.3(3)	-0.73×10^{-4}

The numbers in parentheses are the estimated errors of fitting.

Figure 1. Songhak Yoon *et al.*

Fig. 1. Powder X-ray diffraction patterns of (1) Cr04, (2) Cr08, (3) Cr12, (4) Cr16, (5) Cr40, and (6) Cr60. The diffraction patterns are shown only up to 60° in 2θ for clarity reason.

Figure 2. Songhak Yoon *et al.*

Fig. 2. Raman spectra of (1) Cr04, (2) Cr08, (3) Cr12, (4) Cr16, (5) Cr40, and (6) Cr60. The sharp spikes appearing for Cr60 are originated from cosmic rays, as long exposure times were necessary for this poorly scattering sample.

Figure 3. Songhak Yoon *et al.* **Fig. 3.** (a) Thermogravimetric analysis (TGA), (b) differential thermal gravimetry (DTG), (c) and (d) mass spectrometry (MS) of (1) CrO₄, (2) CrO₈, (3) CrO₁₂, (4) CrO₁₆, (5) CrO₄₀, and (6) CrO₆₀.

Figure 4. Songhak Yoon *et al.*

Fig. 4. (a) Temperature dependence of the susceptibility (χ) (M - T curve) at 0.5 T in the temperature range up to 50 K (inset: full temperature range of 1.8 – 300 K) and (b) M - H curves at 1.8 K (inset: a full magnetization range of (1) CrO₄, (2) CrO₈, (3) Cr₁₂, (4) Cr₁₆, (5) Cr₄₀, and (6) Cr₆₀).

Figure 5. Songhak Yoon *et al.*

Fig. 5. UV-visible diffuse reflectance spectra of (1) Cr04, (2) Cr08, (3) Cr12, (4) Cr16, (5) Cr40, and (6) Cr60.

Figure 6. Songhak Yoon *et al.* **Fig. 6.** Part of the crystal structure, electronic band structure, and density of states (black: total, blue: Cr) for (a) pristine and (b) 12.5% Cr-substituted $\text{Ba}_2\text{In}_2\text{O}_5$. Green, pink, blue, and red spheres represent Ba, In, Cr and O atoms, respectively.

Figure 7. Songhak Yoon *et al.*

Fig. 7. Normalized CO₂ photoconversion rate of Cr-substituted Ba₂(In_{2-x}Cr_x)O₅·(H₂O)_δ and P-25 powders. (Estimated measurement error: $\pm 10\%$)

Figure 8. Songhak Yoon *et al.*

Fig. 8. Master curve of unit cell parameter b , unit cell volume, oxygen and hydrogen contents, Weiss temperature, and Curie constant as a function of Cr substitution.

Supporting information S1.

Figure S1. Flow chart of the setup used for photocatalytic CO₂ reduction. The small picture shows the used reactor beneath the mercury lamp.

Supporting information S2.

Figure S2. Exemplarily chosen XRD reflections of (1) Cr04, (2) Cr08, (3) Cr12, (4) Cr16, (5) Cr40, and (6) Cr60. We observe: i) gradually decreased (020) reflection intensity and total absence for Cr40 and Cr60, indicating the total collapse of superstructure induced by oxygen vacancy ordering, ii) (200) reflection shifts to higher 2θ and merges with the (141) and (002) reflections, iii) significant shifts of the (202) and (080) reflections.

Supporting information S3.

Figure S3. XRD pattern and Le Bail fit of Cr40 (space group *Icm̄m̄*). Observed and calculated diffraction profiles, and the difference plot are shown together with the Bragg positions in short vertical markers.

Supporting information S4.

Figure S4. Raman spectra of samples (a) Cr04, (b) Cr12, (c) Cr16, and (d) Cr40, respectively. The spectra were obtained with a Renishaw InVia Raman microscope using 632.8 nm excitations.

Supporting information S5.

Figure S5. (a) M - H curves at 300 K showing diamagnetic behavior of (1) Cr04, (2) Cr08, (3) Cr12, (4) Cr16, (5) Cr40, and (6) Cr60.

Graphical abstract. Songhak Yoon *et al.*

Highlights:**Cr-substitution in $\text{Ba}_2\text{In}_2\text{O}_5 \cdot (\text{H}_2\text{O})_x$ ($x = 0.16, 0.74$)**

- Cr-substituted and pristine $\text{Ba}_2\text{In}_2\text{O}_5 \cdot (\text{H}_2\text{O})_x$ samples are reproducibly synthesized to elucidate the influence of Cr-substitution.
- The replacement of tetrahedral InO_4 units by octahedral CrO_6 units is responsible for the drastic change of the magnetic and optical properties.
- The UV–vis spectra of the Cr-substituted samples show a bandgap narrowing from 2.88 to 1.80 eV.