

Structural stability and thermal oxidation of CrSBr crystals in air studied at microscopic scales

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ABSTRACT

2D materials with intrinsic magnetic ordering opened new grounds in spintronics and quantum information processing. Out of these CrSBr has been suggested to be an air stable 2D magnet. Herein, we ponder into the mechanisms behind structural stability and thermal oxidation of bulk CrSBr crystals in air. Our XAS and XPS studies show that long-time storage of this material in air produces Br vacancies as well as near-surface defective S and Cr atoms. Experimental AFM, XAS and XPS studies supported by DFT calculations show that heating CrSBr crystals produces vacancies first and then some surface-bound oxides/hydroxides, which increase the surface micro-roughness. In particular, fifteen minutes heating at 270 °C leads to Br and S vacancies as well as presence of sulfates at the surface but without any Cr oxides. However, 15 min heating at 330 °C induces oxidation of Cr atoms into Cr₂O₃ and/or Cr(OH)₃. Furthermore, defective CrSBr undergoes a unique thermal oxidative etching with formation of sub-surface square etch pits. This leads to occasional bursts of the top-most layers once a maximum strain within the CrSBr membrane has been met. The DFT calculations support favorable oxygen incorporation underneath the top-most layers through the Br vacancies and passivation of the S vacancies in the top-most layer.

1. Introduction

2D materials with bulk magnetic ordering are of interest for magneto- and nano-electronics. Out of such materials, many studies have been focused on a narrow range of compounds, namely chromium trihalides (CrX₃). They exhibit antiferromagnetic ordering between the layers in the case of thin crystals and ferromagnetic ordering in the case of bulk crystals [1,2]. Bulk CrI₃ has a Curie temperature of 61 K, but CrX₃ crystals are air sensitive and have flat electronic bands with low carrier mobilities, which limit their applications. Owing to highly dispersive bands in transition metal dichalcogenides (TMDs) a combination of chalcogen and halide atoms has been proposed to improve such limitations. In particular, thin chromium sulfur bromide (CrSBr) has attracted significant interest due to its high Néel temperature of 133 K and dispersive electronic bands [1,2]. Moreover, bulk CrSBr has a direct bandgap of ca. 1.3–1.5 eV [3,4] and strong photoluminescence emission at around 1.25 eV at room temperature [4], which make it a good candidate for optoelectronic applications in ambient conditions.

Knowledge of air-stability and thermally-induced oxidation

mechanisms in 2D materials are of paramount interest for their long-term usage. Time-induced accumulation of defects as well as surface-bound oxides are expected to degrade any devices and to produce new functionalities [5–7]. For example, introducing crystal defects by ion irradiation has been found as an effective way to tune magnetic properties in CrSBr [8]. In addition, calculations have shown that defects such as Cr interstitial defects and their complexes with vacancies produce highly localized electronic states [9]. Br vacancies can also act as a potential donor for n-type doping of CrSBr layers [10].

So far, mechanisms of surface oxidation and etching of 2D materials have been studied thoroughly only in a few isolated cases, such as graphene [11,12] and MoS₂ - the flagship TMD member. The MoS₂ crystals were found to be relatively air stable, with only spontaneous formation of sulfur vacancies [13]. However, upon heating at around 300 °C their surface started to show triangular etch pits together with MoO₃ oxides in the form of sub-nanometric clusters [14,15]. The clusters grew into islands, irregular patches, and amorphous layers at higher temperatures depending on heating conditions [6,16–18] via diffusion limited aggregation [19] and sublimation followed by surface reabsorption [16].

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In contrary to MoS₂, air-stability of CrSBr is still questionable and its thermally-induced oxidation has not been thoroughly addressed. Investigations by optical imaging and Raman measurements showed that multilayered CrSBr flakes do not degrade within a month in air [20]. In addition, electron diffraction patterns showed that thin CrSBr flakes keep their symmetry after several months of air-exposure and upon heating at 250 °C [21]. However, in another study [22] it has been found that mechanical exfoliation of CrSBr in air degrades the quality of the produced monolayers and suppresses their characteristic Raman peaks. Moreover, 55 day air-exposure produced defect peaks in Raman spectra of mono- and few-layered CrSBr samples. Such peaks have been attributed to Br defects in all studied samples as well as Cr and S defects found mostly in their monolayers [23]. Presence of such defects was also suggested in bulk CrSBr crystals from a non-monotonic behavior of their mechanical properties vs. indentation depth [24].

In this study, we shed more light on microscopic stability of CrSBr crystals in air as well as ponder into the mechanisms of their thermally-induced oxidation. We use bulk-sensitive X-ray adsorption spectroscopy (XAS) and surface-sensitive X-ray photoelectron spectroscopy (XPS) to reveal any defects and oxides onto freshly exfoliated as well as one-year old CrSBr crystals stored in air. Next, we expand our studies to use a combination of XAS, XPS and high-resolution atomic force microscopy (AFM) measurements to ponder into oxidation of air-heated CrSBr samples. Finally, we use the density functional theory (DFT) simulations to complement our experimental findings.

2. Materials and methods

2.1. Exfoliation and heating of CrSBr crystals

Laboratory-grade bulk CrSBr crystals were bought from HQ graphene, Groningen, Netherlands. Nitto tape (ELP BT-150E-KL) was used for mechanical exfoliation and exposure of fresh crystal surface to air. For heating, the samples were placed on a Si/SiO₂ substrates bought from MicroChemicals GmbH, Germany. The substrates were ultrasonically cleaned in deionized water, acetone, ethanol and finally isopropanol for 10 min each. After each ultrasonication step, the substrate was dried in pure argon. Samples were heated in air for 15 min at each specified temperature except for the sample noted as “300 + 330 °C”, which was heated first at 300 °C for 15 min and then at 330 °C for another 15 min. A standard hot plate, Thermo Scientific, product no. HP88854105 was used. During heating, the samples were covered with a quartz Petri dish to ensure a controlled atmosphere and proper distribution of temperatures within a heating zone. A standard thermocouple and a Pt thermometer were used to calibrate the temperature with a temperature error of ±2 °C.

2.2. AFM topography imaging

A Cypher S AFM was used in tapping mode with AC160TS-R3 cantilevers (Asylum Research) for sample topography imaging. Raw data were treated with the Gwyddion software (v.2.51, Czech Metrology Institute, Brno, Czech Republic). Standard line-by-line first or second-order horizontal flattening together with removal of occasional glitches were applied.

2.3. XAS measurements

The chemical state and local structure of the CrSBr samples were examined using the near edge X-ray absorption fine structure (NEXAFS) measurements. NEXAFS spectra were collected at a custom-made STXM end station, designed by Dr. T. Tyliczszak, at the Solaris National Synchrotron Radiation Centre in Cracow, Poland. The beam parameters involved a photon energy range of 100–2000 eV with a relative energy resolution ($\Delta E/E$) not worse than 0.001, beam diameter of less than 100 nm and a photon flux at sample of 10^9 – 10^{12} [pH/s/100 mA]. The energy

step size around the absorption peaks was 0.2 eV.

2.4. XPS measurements

XPS data were recorded on Kratos Axis Supra spectrometer, equipped with a monochromatic Al K α radiation source (1486.7 eV) operating at 375 W. Analyzer pass energies for the survey spectra were 160 eV and for all other spectra were 40 eV. The instrument work function was calibrated to obtain a binding energy of 84.0 ± 0.1 eV for the 4f_{7/2} line of metallic gold. The spectrometer dispersion was adjusted to yield a binding energy of 932.6 eV for the Cu 2p_{3/2} line of metallic copper. A flood gun was used for charge neutralization of the heated sample. The binding energies of the spectra were calibrated by C 1s core line position at 284.8 eV. A mixed Gaussian (70%)–Lorentzian (30%) function after a Shirley background subtraction was used for spectra fitting. Spectra were analyzed using the CasaXPS software (version 2.3.26rev1.2Y).

2.5. DFT calculations

Spin-polarized calculations were done with the code VASP6 [25,26]. The PBE exchange and correlation functional was adopted [27], along with the dumped D3 force field for long-range dispersion [28,29]. The plane-wave basis set was truncated with a kinetic energy cutoff of 520 eV. The reciprocal space was sampled with a Γ -centered mesh of k-points of 8x8x2 [30]. Tight convergence criteria were adopted for the electronic (10^{-5} eV) and ionic (10^{-2} eV/Å) loops. The core-valence interaction was treated with the Projector Augmented Wave approach [31], treating O(2 s,2p), S(3 s,3p), Br(4 s,4p) and Cr(4 s, 3d) as valence states. The adsorption of oxygen, and subsequent reactive steps were simulated on a CrSBr 2x2x2 supercell with a mesh of 4x4x1 k-points. A 25 Å-thick vacuum layer was included in the supercell. Dipole and quadrupole corrections were applied along the non-periodic direction. An A-type antiferromagnetic ordering was set in pristine CrSBr, in agreement with a previous joint computational and experimental report [1]. An initial 4s⁰ 3d³ electron configuration was set on each Cr atom, and almost retained, yielding magnetic moments close to 3 μ_B at the end of the relaxation. The formation energy of defects was calculated with respect to the pristine material and the most thermodynamically stable forms of elementary bromine (Br₂ molecule) sulfur (S₈ molecule) and chromium (bulk metallic Cr), as follows:

$$E(V_{Br}) = E(CrSBr_{1-x}) + \frac{1}{2}E(Br_2) - E(CrSBr)$$

$$E(V_S) = E(CrS_{1-x}Br) + \frac{1}{8}E(S_8) - E(CrSBr)$$

$$E(V_{Cr}) = E(Cr_{1-x}SBr) + \frac{1}{2}E(Cr_{bulk}) - E(CrSBr)$$

3. Results and discussion

To start pondering about changes in chemical composition of the CrSBr bulk crystals during their long-time storage, we performed XANES studies on freshly exfoliated (“fresh”) and ca. one-year air-exposed (“old”) samples. Then, we extended the XAS studies to the fresh samples heated in air. We concentrate on Cr peaks within our accessible energy range, i.e., the Cr L₂ and L₃ X-ray adsorption edges, see Fig. 1(a). We also notice that an instrumental peak at 592.6 eV is present on all Cr spectra. It is marked with an asterisk and has been used as a calibration peak.

Regarding the non-heated samples, we notice that shapes of the obtained Cr edges are very similar to prior Cr³⁺ XAS spectra collected on CrSBr [32], as well as on other similar compounds such as CrSiTe₃ [33,34], and CrGeTe₃ [35]. Therefore, the peaks at 577.4 ± 0.1 eV and 585.6 ± 0.1 eV for the old and fresh samples in Fig. 1(a) are ascribed to the Cr L₃ and L₂ edges in CrSBr [32]. Furthermore, the XAS spectra for these samples are almost the same and do not show any distinguishable

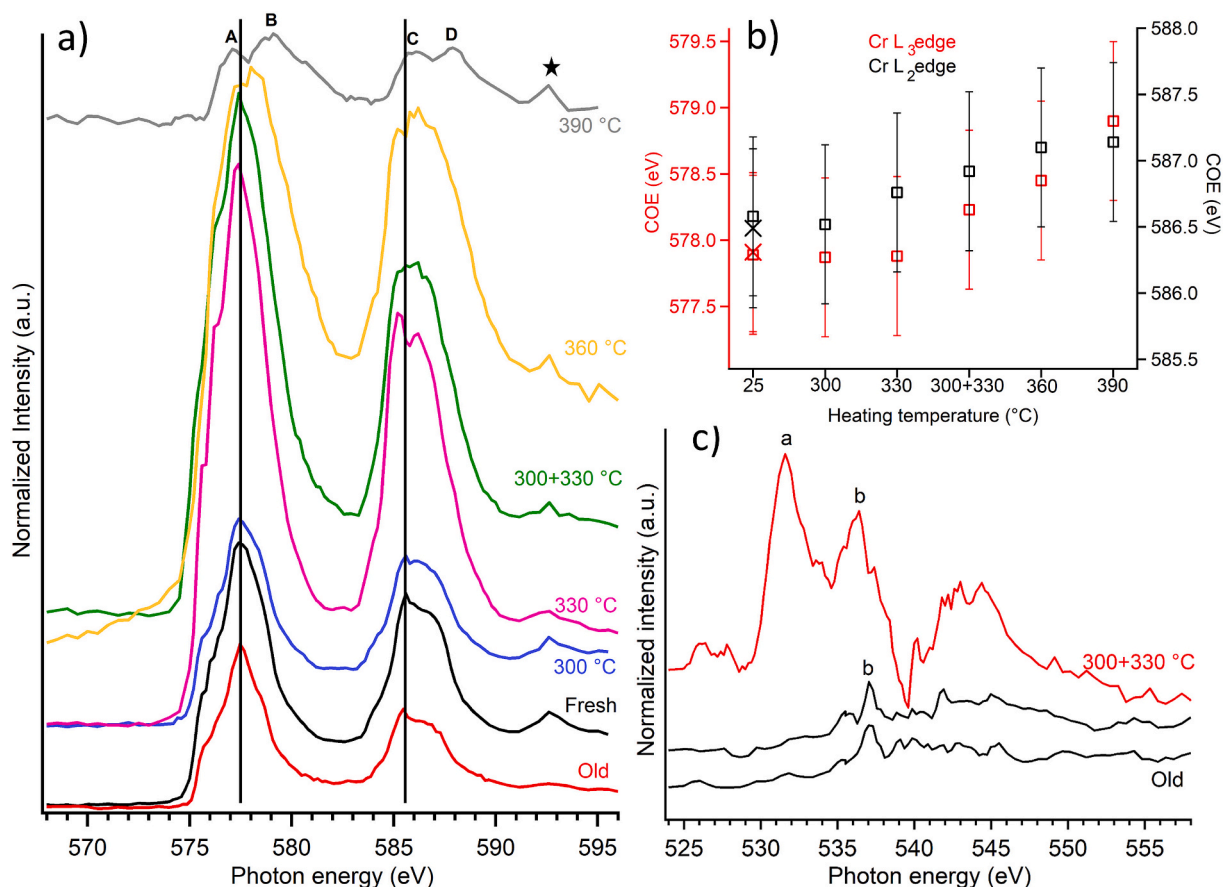


Fig. 1. XAS studies on bulk CrSBr crystals: (a) Cr $L_{2,3}$ edge spectra. Black lines mark absorption peaks in unheated samples. (b) Center of energy (COE) versus heating temperature for Cr L_3 and L_2 edges. Crosses refer to old (unheated) samples and squares refer to fresh samples. The error bars arise from the law of propagation of errors in energy. (c) Oxygen K edge spectra.

effects of long-term storage in air.

Next, we move to the Cr XAS spectra collected on air-heated samples. Interestingly, the Cr spectrum after heating at 300 °C is still the same as in the case of the non-heated samples. However, by heating at 330 °C and more, the shapes and positions of the Cr L_2 and L_3 edges start to change. The most prominent changes are visible at 390 °C. To quantify them, we calculate the center of energy (COE) for the Cr L_2 and L_3 edges by an analogous formula as used for the center of mass. This is done by summing up the products of energies (lateral axis) and their corresponding intensities (vertical axis) and then dividing the result by summed intensities for all the points within each absorption edge. The obtained COEs for L_2 and L_3 edges are shown in Fig. 1(b). For the sample heated at 330 °C, only the COE of its L_2 edge shows a noticeable increase. For the sample heated at 360 °C, both COEs have already increased. For the sample heated at 390 °C, both COEs have increased further. Therefore, we conclude that 330 °C marks an onset of the observed changes for the chosen here 15 min heating time. We did not study extensively the cumulative time and temperate effect. However, additive changes in the sample heated first at 300 °C and then at 330 °C should be more than in the samples heated separately at these temperatures. And indeed, this is observed in the case of the sample “300 °C + 330 °C”.

An increase in the COE values with temperature means that higher energy photons are absorbed by the Cr 2p electrons indicating that the outer shell electrons have been pulled away from the nucleus. Such a phenomenon can arise from incorporation of atoms with higher electronegativity than S and Br within a close environment of the Cr atoms. Due to heating in air, nitrogen and oxygen containing species should be considered in this respect, out of which incorporations of atomic oxygen

and OH^- groups are the most likely scenarios. Therefore, the results of heating at 330 °C might indeed show some first traces of Cr oxides/hydroxides.

Similar conclusions can be drawn from the evolution of the absorption peaks and their shapes. On one hand, the black vertical lines in Fig. 1(a) mark two absorption peaks for non-heated CrSBr. They are the same as in the case of the samples heated at 300 °C. On the other hand, there are four major peaks in the XAS spectrum of the sample heated at 390 °C. They are marked as A, B, C, D and match the XAS spectra of Cr_2O_3 and/or $\text{Cr}(\text{OH})_3$ in Ref. [36]. Regarding the samples heated above 300 °C, one can observe a gradual transition from two to four energy peaks, indicating a measurable presence of Cr(III) oxides/hydroxides. Noteworthy, the extremely small differences between Cr_2O_3 and $\text{Cr}(\text{OH})_3$ reported in Ref. [36] are not resolvable in our experiments. Therefore, we cannot distinguish between these two chemical species.

To complement the discussion about oxide/hydroxide formation, we take a careful look on the oxygen K edge, see Fig. 1(c). Therein, a peak at 536.5–537 eV (named “b”) is visible in all spectra. Thus, we associate it with the surface adsorbed oxygen species. However, the sample heated progressively to 330 °C shows a strong peak at 532 ± 0.1 eV (named “a”), which has been observed in prior works as a strong indicator of the oxides [14,36]. This is another prove of the surface-bound Cr oxides/hydroxides, which start to be visible at 330 °C.

To address whether oxides/hydroxides produce any visible morphological changes at a surface of the CrSBr crystals, we performed high-resolution AFM topography studies. Figs. 2(a–c) show the topography images of a $3 \mu\text{m}^2$ CrSBr surface after its several heating stages. The sample after exfoliation shows a very flat surface with the root mean square roughness (Sq) and the mean roughness (Sa) of only 17 and 13

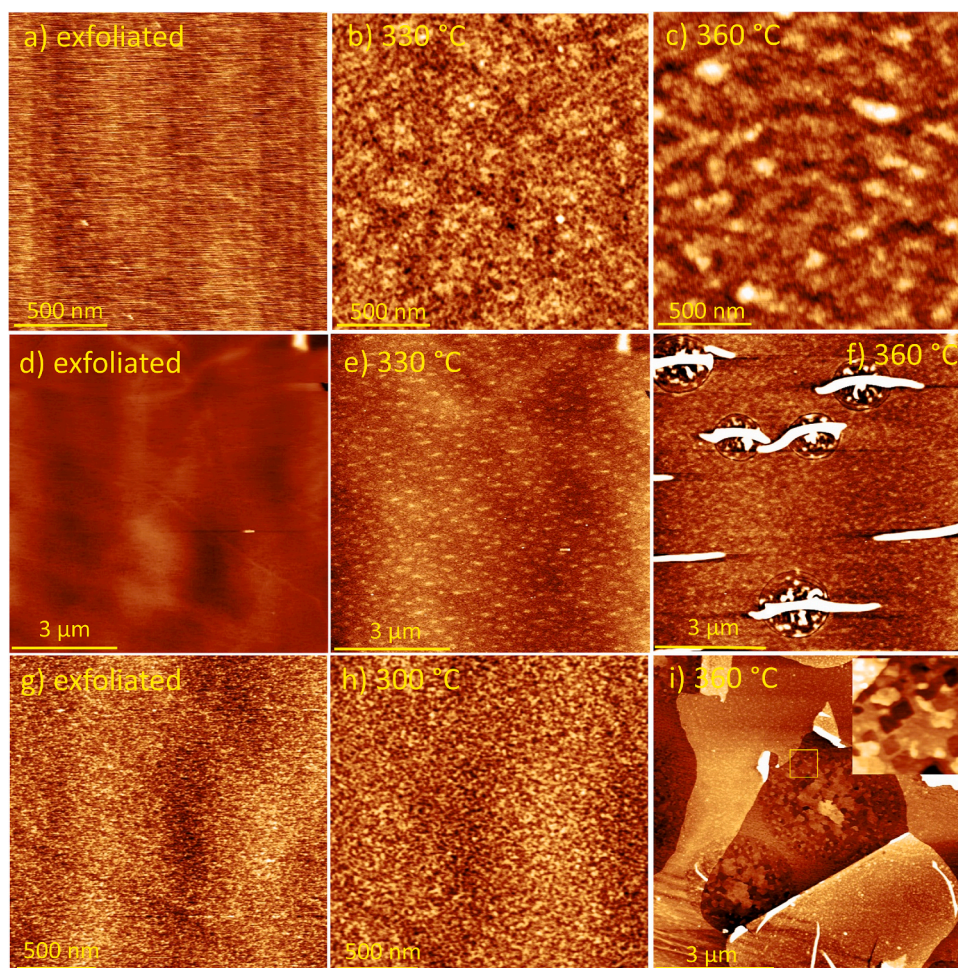


Fig. 2. High resolution AFM studies on bulk CrSBr surfaces: Topography images of (a-c) ca. $3 \mu\text{m}^2$ -wide, (d-e) ca. $81 \mu\text{m}^2$ -wide, and (g-h) ca. $3.6 \mu\text{m}^2$ -wide CrSBr surfaces. (i) A topography image of a bulk CrSBr sample after heating at 360°C . Z-scales in (a-i) are 130 pm, 797 pm, 2.3 nm, 2 nm, 2 nm, 3 nm, 394 pm, 800 pm, and 14.6 nm, respectively. Higher colors represent higher heights. Inset in (i) shows a magnified portion of the image (marked with yellow square) with square etch pits. Z-scale is 5.8 nm. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

pm, respectively. Heating at 330°C altered its surface morphology and increased the values of S_q and S_a up to 101 and 80 pm, respectively, which is six times larger than before. This is similar to previous AFM topography studies on thick CrSBr flakes [37]. Further heating at 360°C roughened the surface even more to yield S_q and S_a of 300 and 226 pm, respectively. Figs. 2(d-f) show the same progression of heating steps on the same sample but over a larger area. Therein, changes in the surface morphology due to heating are even more visible. In particular, elongated grain-like features appear after heating at 330°C and circular features with elongated rods start to be visible after heating at 360°C . We speculate that observed roughness increases as well as new topographical features appearing at 330°C are related to oxide formation on the surface. This matches our earlier XAS findings showing Cr oxides forming around 330°C . Moreover, quite likely due to substantial differences between crystal lattices of Cr_2O_3 and CrSBr, i.e., hexagonal vs. orthorhombic, the deposits in Fig. 2(f) are elongated and unable to match an underneath CrSBr structure.

Small scale topography images of the same $4 \mu\text{m}^2$ area within the bulk sample before and after heating at 300°C are shown in Figs. 2(g,h). Therein, we observe only a two-fold roughness increase from the values of S_q and S_a being 55 and 44 pm to 102 and 82 pm, respectively. Comparing Figs. 2(a,b) with (g,h), one does not observe any meaningful change in surface morphology after heating at 300°C . This is also visible in topography images of a bigger area, shown in Fig. S1. The small roughness change without any change in topography might relate to

formation of surface vacancies. In particular, formation of Br vacancies is a necessary step to expose the S and Cr atoms for their oxidation.

Furthermore, we spot the sub-surface oxidative etching onto AFM topography images of the old CrSBr samples after heating them at 360°C , see Figs. 2(i) and S2, which according to our knowledge has not been previously observed. Therein, one can see two distinct features: bursts within the top-most CrSBr layers as well as sub-surface etch pits within the burst zones. The burst zones are either oval or circular and expose underlying circular areas with etch pits.

The square-like etch pits are well visible on the inset in Fig. 2(i). These pits are a sign of oxidative etching with a complete removal of the products. Their square-like shape is a direct reflection of the orthorhombic CrSBr crystal structure. For comparison, the etch pits in MoS_2 are triangular, due to its hexagonal crystal structure, and occur within the top-most layers. Very interestingly, we did not observe any oxidative etch pits on the top-most CrSBr layer. However, we have observed grain-like and circular top-most surface features on the oxidized CrSBr in Fig. 2(f). We also note that in order to provoke any etching, some oxygen species must have penetrated underneath the sample, likely through defects within the top-most CrSBr layers located at the center of the circles. The circular shape of the zone with etch pits means that these oxygen species must have spread equally in all lateral directions.

In order to complement our XAS and AFM results, we conducted XPS studies on the CrSBr samples. We start by discussing the non-heated samples. Fig. 3 shows the XPS spectra of C 1 s, O 1 s, S 2p, and Cr 2p

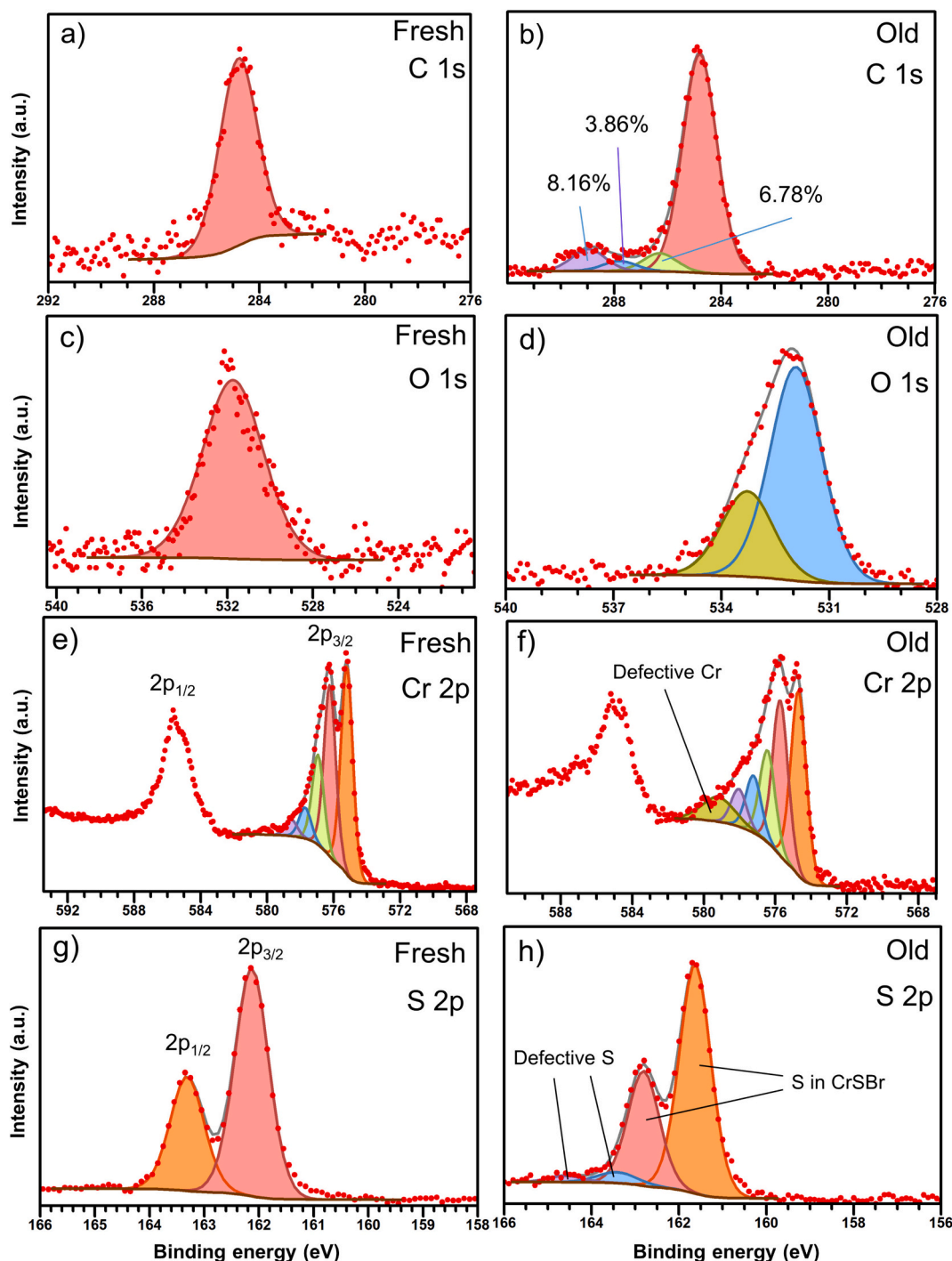


Fig. 3. XPS studies on fresh and old bulk CrSBr surfaces. (a,b) C 1s, (c,d) O 1s, (e,f) Cr 2p, and (g, h) S 2p spectra.

in fresh and old samples. The fresh sample shows a small carbon peak at 284.8 eV, which is attributed to adventitious carbon (C—C, C—H bonds) [15,38]. However, the old sample shows a larger adventitious carbon peak along with few smaller peaks at 286.3, 287.8 and 288.9 eV, which are attributed to carbon in C—O, C=O and O—C=O groups, respectively [38–40]. Regarding oxygen, the fresh sample shows a small peak at 531.7 eV indicating surface adsorbed OH groups [17,41]. However, the old sample shows two considerable peaks at 531.9 and 533.3 eV. Herein, the peak at 531.9 eV can indicate surface adsorbed OH groups like in the case of the fresh sample, but based on the carbon spectra this peak can also be attributed to oxygen in CO groups as well as one of the oxygens in O—C=O group [40,42]. Finally, the 533.3 eV peak can be attributed to

another oxygen in the O—C=O group [40,42] and physisorbed water [39]. The O 1s spectrum of the old sample lacks as well any sign of oxygen within the Cr oxide lattice, i.e., a peak below 531 eV [43].

Regarding chromium, the Cr 2p_{3/2} XPS spectra of the fresh and old samples are shown in Figs. 3(e,f), respectively. Both raw spectra show a similar structure with two peaks, characteristic of Cr in various Cr(III) compounds [37,43]. The Cr 2p_{3/2} spectrum of the fresh sample is perfectly fitted with five peaks at 575.2, 576.2, 576.9, 577.7, and 578.5 eV. The Cr 2p_{3/2} spectrum of the old sample can also be fitted with five peaks with the same differences in their binding energies as in the case of the fresh sample. The peak positions are now at 574.7, 575.7, 576.4, 577.2, and 578.0 eV. Due to substantial carbon contaminations this Cr

$2p_{3/2}$ spectrum is more noisy and redshifted by 0.5 eV with respect to the fresh sample. Finally, a new peak at 579.2 eV emerged for the old sample, and we ascribe it to defective Cr atoms at higher oxidation states than +3.

Regarding sulfur in Figs. 3(g,h), two peaks at 162.1 and 163.3 eV are visible in the fresh sample, which are attributed to $S\ 2p_{3/2}$ and $S\ 2p_{1/2}$ in $CrSBr$, respectively. In the case of the old sample, these peaks are located at 161.6 and 162.8 eV showing a similar red-shift discussed above for the Cr spectrum. However, two new peaks at 163.4 and 164.6 eV emerge in the spectrum of the old sample. Their necessity is further discussed within supporting information and Fig. S3. They are attributed to defective sulfur, which could be S atoms bonded to surface adsorbed species. Such an outcome becomes possible only after creation of Br vacancies to expose the S atoms. Thus, it is an indirect prove for the presence of the Br vacancies. Finally, the shape of the Br XPS spectra is the same for both samples, see Fig. S4 in the supporting information. Moreover, the Br spectrum of the old sample shows the same slight red-shift as described earlier in Cr and S spectra, which confirms the C contamination origin of this shift.

In order to confirm the presence of Br vacancies as well as check for the potential sulfur vacancies, Br/Cr and S/Cr ratios have been calculated based on Cr 2p, S 2p, and Br 3p at.% detected in XPS survey spectra, see Fig. S5. The calculated Br/Cr ratios in the fresh and old samples are 12.9 and 3.3, respectively, which indicates a substantial increase in the number of Br vacancies upon air-exposure. However, the calculated S/Cr ratios in the fresh and old samples are 2.8 and 3.0, respectively, indicating no measurable change in the number of sulfur vacancies.

Now, we discuss the XPS spectra obtained on the heated samples, see Fig. 4. We start with the ones collected after heating at 270 °C. First, the S 2p spectrum in Fig. 4(a) shows two previously observed peaks from S^{2-} in $CrSBr$ at 162.0, 163.2 eV, as well as two new peaks at 168.8 and 170.0 eV, which are associated with S^{6+} in sulfates [44–46]. Second, the O 1s spectrum of this sample, see Fig. 4(b), shows a peak at 531.4 eV, which can be attributed to surface-adsorbed OH groups and oxygen in sulfates [44]. Third, the Cr $2p_{3/2}$ spectrum of this sample shows a similar double-peak structure as in the fresh $CrSBr$, see a blue arrow in Fig. 4(c). Consequently, we fit this spectrum with five peaks with almost the same positions as in the fresh $CrSBr$. These are at: 575.0, 576.0, 576.7, 577.5, and 578.3 eV. In addition, a sixth peak at 579.1 eV emerged for this sample, which can be ascribed to defective Cr atoms as in the case of the

non-heated old sample as well as some traces of Cr sulfates. Finally, the Br/Cr and S/Cr atomic ratios are calculated from the XPS survey spectra, see Fig. S6. Br/Cr and S/Cr ratios are 0.9 and 0.7, respectively. These ratios are considerably lower than in the fresh sample, which indicates formation of both Br and S vacancies upon heating.

Next, we discuss the XPS results from the sample heated at 330 °C, which we found earlier as the onset temperature for Cr oxide/hydroxide formation. The S 2p spectrum of this sample is presented in Fig. 4(d). Comparing with the sample heated at 270 °C, it shows the same four peaks but now at 162.3, 163.5, 169.2 and 170.4 eV. The former two are from S^{2-} in $CrSBr$ and latter two originate from S^{6+} in sulfates. However, the S^{6+}/S^{2-} ratio has increased with temperature. The O 1s spectrum presented in Fig. 4(e) clearly shows two peaks at 532.3 and 530.5 eV. The peak at 532.3 eV can originate from oxygen in sulfates [44,47], while a new peak at 530.5 eV is ascribed to oxygen in Cr_2O_3 and/or Cr (OH)₃ [43]. Regarding the Cr 2p, the sample heated at 330 °C lacks any sign of the multiplet structure, see Fig. 4(f), but rather shows a broad peak at 577.3 eV. In comparison to all previous studied samples, this peak is shifted to higher energy. The peak broadness and its position match the $Cr(OH)_3$ at 577.3 eV [43] and/or Cr_2O_3 at 576.6–577.2 eV [43,48]. In addition, we show the absence of nitrogen within this heated sample, see Fig. S7. Finally, the old sample from Fig. 3 was also heated at 330 °C and investigated by XPS. The results are in Fig. S8 and show the same qualitative oxidation outcomes as discussed above.

Overall, the XPS data for both non-heated samples lack any Cr oxides. Furthermore, the old sample shows an increased number of Br vacancies but not S vacancies with respect to the fresh sample. The old sample displays as well some defective Cr and S atoms. Regarding the effects of heating, the sample heated at 270 °C still does not have any Cr oxides but shows some sulfates and defective Cr atoms. Moreover, heating at this temperature produces some Br and S vacancies. However, the sample heated at 330 °C presents some surface Cr(III) oxides and/or hydroxides as well as higher amounts of sulfates. In addition, we also show that heating in air up to 330 °C does not provoke any nitrogenation of the $CrSBr$, which is similar to MoS_2 and implies that harsher conditions such as plasma or lithographic treatments are needed for their possible nitrogenation [5,49].

Raman measurements were also performed on fresh, old and heated samples to examine the structural stability of bulk $CrSBr$. All the samples showed characteristic A_g^1 , A_g^2 and A_g^3 Raman peaks at 114.9, 245.8 and 343.9, respectively, see Fig. S9. No unique sign of oxides or defect peaks

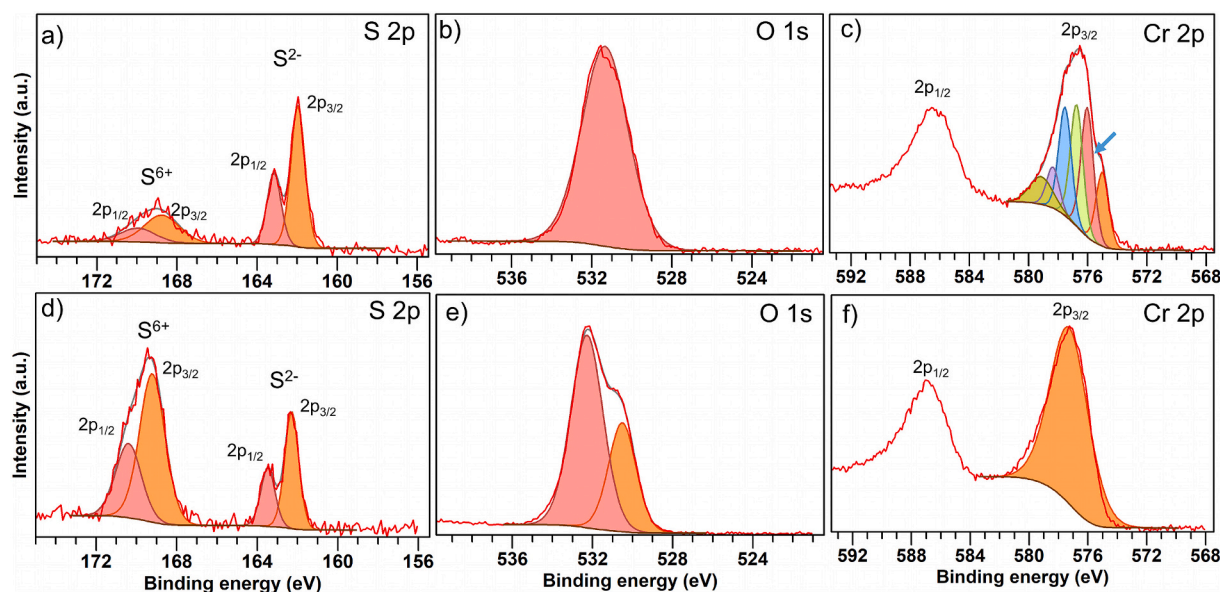


Fig. 4. XPS studies on heated $CrSBr$ samples. (a and d) S 2p, (b,e) O 1s, and (c,f) Cr 2p of the bulk $CrSBr$ samples after heating at 270 and 330 °C for 15 min, respectively.

were observed in old and heated samples. Since the Raman signal comes from many layers, it shows that the defects and oxides observed in XPS and XAS studies were not extended to the inside of the bulk CrSBr samples.

DFT calculations on a CrSBr bilayer strengthen our experimental observations, and permit to complement them with some mechanistic insight. At first, we report that oxygen molecules are only weakly physisorbed on the outer surface of the defect-free CrSBr, with a respective formation energy of $E_{\text{ads}} = -0.11$ eV, see Fig. 5(a). The intercalation of an O_2 molecule in the interlayer spacing is even endothermic with a formation energy of $+0.86$ eV, see Fig. 5(b). Hence, the O_2 molecule is so weakly adsorbed that it would interact with the outer surface only at very low temperature. On the contrary, dissociative adsorption of O_2 leads to a thermodynamically stable structure, Fig. 5(c), where O atoms are bridging Cr and S sites. The dissociative adsorption, however, is hindered by a very large kinetic barrier of 2.61 eV, see the surface pristine path in Fig. 6. Since penetration in the interlayer is thermodynamically hindered, one can thus infer that defect-free CrSBr is scarcely prone to oxidative etching, in particular in the sub-surface region.

The picture, however, is quite different on defective CrSBr. The calculated formation energies of single point vacancies on the outer CrSBr surface are: 2.50 eV for Br vacancy (V_{Br}), 2.86 eV for S vacancy (V_{S}) and 3.46 eV for Cr vacancy (V_{Cr}). These values almost do not change if the same point defects are created on the inner surface, and we get 2.61 eV for V_{Br} , 2.90 eV for V_{S} and 3.44 eV for V_{Cr} . Thus, one observes that formation of Br and S vacancies is much more favorable than in the case of Cr vacancies, both in the outer and inner surfaces. For this reason, we did not consider Cr vacancies in the oxidation process. The possibility of aggregation of single vacancies into larger defect complexes, as observed after electron beam irradiation [9], cannot be entirely ruled out. According to DFT calculations on a twice larger

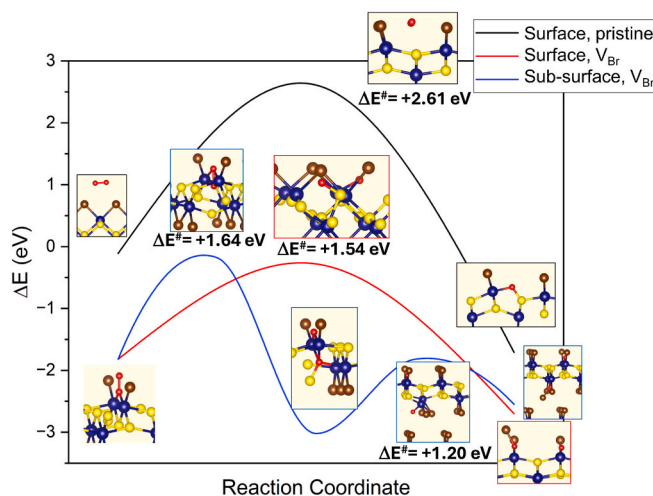


Fig. 6. Calculated energetic pathways for surface and sub-surface oxidative etching on pristine and Br-vacant CrSBr.

supercell, see Table S1 in the supporting information, the formation of a double vacancies is almost thermo-neutral with respect of the formation of two single vacancies. A strong energy gain for defects clusterization was reported only when the creation of an unfavorable V_{Cr} is accompanied by the removal of some of the surrounding S and Br anions. However, such formation energies for all kinds of combined defects are much above the formation energy of a single V_{Cr} and therefore we do not consider them in further oxidation analysis.

The adsorption of oxygen on a V_{Br} site on the outer CrSBr surface yields -1.82 eV formation energy, see Fig. 5(d). The O_2 molecule is

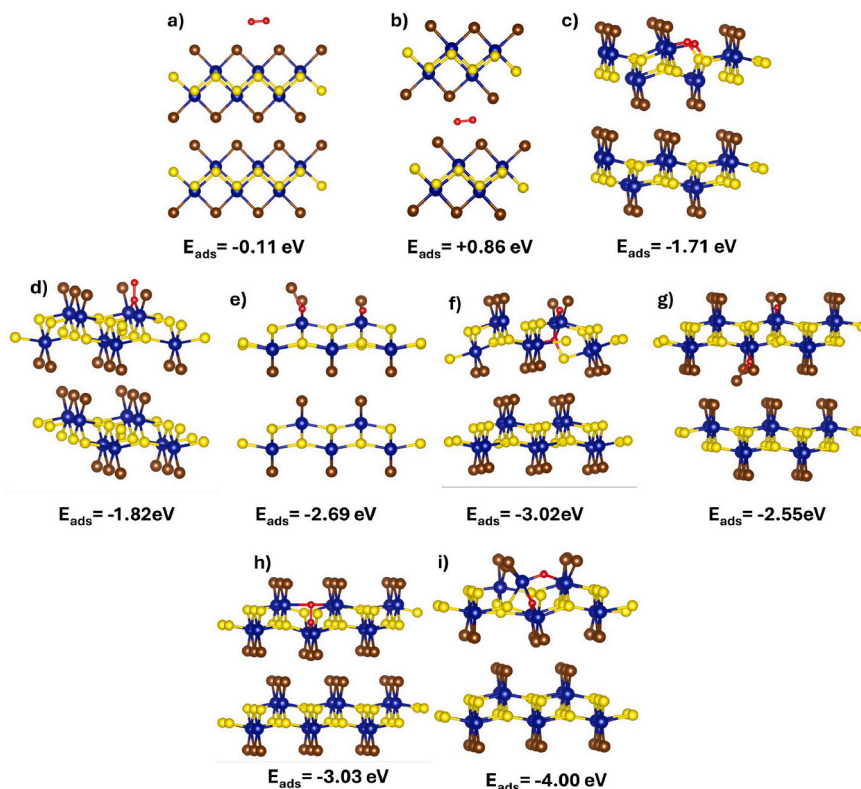


Fig. 5. Ball-and-stick view of DFT calculated structures with respective formation energies. (a) O_2/CrSBr , top-most (outer) surface, (b) O_2/CrSBr , inner surface. (c) Dissociative adsorption on CrSBr. (d-e) O_2 splitting and etching on the surface of CrSBr_{1-x} . (f-g) O_2 splitting and etching on the sub-surface of CrSBr_{1-x} . (h-i) $\text{O}_2/\text{CrS}_{1-x}\text{Br}$. The energies, E_{ads} , are reported with respect to CrSBr and gas-phase O_2 molecule. Br: brown, S: yellow, Cr: blue, O: red. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

bound at the defect and strongly activated since the O—O distance is increased to 1.32 Å with respect to 1.23 Å in the gas phase. One can envisage that this structure is the starting point for two different oxidation pathways, leading either to surface or sub-surface oxidative etching. Surface etching, where the oxygen molecule fully dissociates and one O atom displaces a Br atom from a neighboring lattice site, Fig. 5(e), implies a remarkable thermodynamic gain of -2.69 eV with respect to the reactants. The kinetic barrier is 1.54 eV, see the surface V_{Br} pathway in Fig. 6, which also is substantially smaller compared to the pristine CrSBr. Alternatively, starting from an O_2 molecule adsorbed on the V_{Br} site, Fig. 5(d), one could envisage an oxygen diffusion through the CrSBr layer. This leads to a stable intermediate with a formation energy of -3.02 eV, see Fig. 5(f), where an S atom is initially displaced from its lattice site. This structure is reachable through a comparable kinetic barrier of 1.64 eV, see the sub-surface V_{Br} pathway in Fig. 6. A further diffusion step could lead the O atom to occupy a Br lattice site, -2.55 eV in Fig. 5(g), overcoming a moderate barrier of 1.20 eV, see Fig. 6. Notably, the interlayer distance increases from 2.30 Å in pristine CrSBr to 2.76 Å in the presence of an extra-lattice/displaced bromine atom like in Fig. 5(g). This certifies the remarkable strain exerted on the topmost CrSBr layer in the sub-surface diffusion scenario.

A V_S site on the outer surface is also a favorable trapping site for O_2 molecules with $E_{ads} = -3.03$ eV with respect to $CrS_{1-x}Br$ and gas-phase O_2 , see Fig. 5(h). The elongation of the O—O distance (2.45 Å) is even larger compared to the case of an O_2 molecule on V_{Br} . A remarkable energy gain of 0.97 eV (-4.00 eV with respect to $CrS_{1-x}Br$ and gas-phase O_2) is associated with the splitting of the adsorbed oxygen molecule, leaving an O atom in the previous V_S site, Fig. 5(i). The second O atom is trapped in the CrSBr layer. Different to the V_{Br} case, no feasible path has been identified toward any further transfer of the O species to a Br lattice site, and the release of Br species in the interlayer.

We thus conclude that V_{Br} sites are the most likely type of defects acting as an initial gateway to oxygen penetration and sub-surface oxidative etching. The V_S sites, on the contrary, will most likely be poisoned by the incoming atmospheric oxygen, without promoting any further structural changes and sub-surface etching. This aligns with experiments where the sub-surface oxidative etching was observed by AFM only on the old sample after heating at 360 °C and not the fresh sample after the same heating procedure. As showed by XPS studies only the number of Br vacancies was increased at room temperature due to air storage.

To further compare with experiment, we suggest that the few oxygen atoms underneath the surface in a confined environment are an effective etchant at sufficiently increased temperature. This is particularly plausible in the case of Br atomic vacancies in the inner layer. Their presence is suggested in our DFT results and has been experimentally confirmed in Ref. [9] At the same time, more numerous oxygen atoms at the surface produce oxides at increased temperature. However, we did not observe any square etch pits on the CrSBr surface. A tentative explanation could involve some analogies to MoS_2 oxidative etching in air. In that case, the etch pits (triangular therein) were obtained only at relatively low temperatures, e.g., usually 300 °C. In contrary, MoS_2 samples heated above 500 °C did not show any etch pits, but only irregular patches containing MoO_3 [6]. The latter was attributed to vigorous oxidation with accumulation of surface oxides, which blocked the reaction progress along preferential crystallographic directions. The former was attributed to slower oxidative etching where any produced oxides left the surface and did not block formation of etch pits [6]. Therefore, by analogy, we suggest that surface CrSBr oxidation proceeds faster and with creation of some surface-bound oxide molecules hindering the etch pit formation, while the sub-surface etching proceeds slower and with oxides being able to detach from the developing etch pits.

Finally, we concentrate on the mechanistic insight into the surface bursts, which are the consequence of the sub-surface etching, see Fig. 2(i). We suggest that such bursts originate from gases, which accumulated underneath the surface and were later released once the inside pressure

surpassed a mechanical threshold. To get a simple estimate of such inside pressure we assume a complete etching of one CrSBr layer within the bubble. Noteworthy, this would yield an asymptotic upper limit since such a complete etching would result in one large etch pit covering a total area underneath the bubble. For calculations, we consider the unit cell of CrSBr having two Br, two Cr, and two S atoms within an orthorhombic structure with lateral lattice constants $a = 0.35$ nm, and $b = 0.47$ nm [50]. Based on CrSBr chemistry and our XPS studies we assume that the gases are Br_2 and SO_2 . Thus, for a central burst area of $14.84 \mu m^2$ in Fig. 2(i), we obtain 14.84×10^{-17} mol of Br_2 and 29.68×10^{-17} mol of SO_2 . They are confined in a cylindrical volume with thickness of 1.2 nm, which is one etched CrSBr layer and a van der Waals gap of half the layer [51]. The pressure, p , of these trapped gases is obtained from the van der Waals equation: $p = \frac{nRT}{V-nb} - \frac{an^2}{V^2}$. Therein, n is the number of gas moles, V is the volume, T is the absolute temperature, R is the universal gas constant of $8.3144 J \cdot mol^{-1} \cdot K^{-1}$, and a , b are substance-specific constants. We get tabular values of a as 9.75 and $6.865 \text{ bar} \cdot L^2 \cdot mol^{-2}$ and of b as 0.0591 and $0.05679 L \cdot mol^{-1}$ for Br_2 and SO_2 , respectively [52]. Considering V of $17.81 \times 10^{-21} m^3$ and T of 633 K, the obtained upper limit of the inside pressure is 1.46 GPa. However, this value is unphysical since at such conditions the Br_2 is already at a supercritical regime [53]. Moreover, we did not even consider any solid Cr_2O_3 , which would further increase the aforementioned pressure.

Fast pressure increase within the bubble would cause it to rupture much before the CrSBr layers within it are completely etched, which we also experimentally observed. Therefore, we estimate the rupture pressure utilizing the membrane mechanics and the maximum strain, which a given membrane can sustain. In this regard, the inside pressure within a membrane can be obtained from the Hencky's model [54,55], which calculates the pressure difference, ΔP , between inside and outside of the membrane as: $\Delta P = Et \frac{2}{1-\nu} \frac{h^2}{a^2}$. In this formula, E is the Young's modulus, t is the thickness, ν is the Poisson's ratio, h is the height of the bubble, and a is its radius. To calculate the membrane rupture pressure, ΔP_{max} , we need to obtain the value of h just before the bubble rupture, which could not be measured directly. Therefore, we estimate it from the maximum mechanical strain inside the membrane. This in turn can be estimated by Föppl-von Kármán equation assuming that the bubble edge is fully clamped at the bubble substrate [54]. Therein, the maximum radial (ϵ_r) and circumferential (ϵ_θ) strains present at the top of the bubble are the same and calculated as $\epsilon_{max} = \epsilon_{r=0} = \epsilon_{\theta=0} = \frac{h^2}{4a^2} (3 - \nu)$. Supposing that thin CrSBr membranes can sustain similar maximum strain and have the same Poisson's ratio as MoS_2 , we can calculate the membrane rupture pressure. Using $\epsilon_{max} = 0.11$ [56], $\nu = 0.3$ [57], as well as $E_{CrSBr} = 45$ GPa [24] yields ΔP_{max} of 0.01 GPa for the bubble burst in Fig. 2(i) with $a = 2.17 \mu m$ and $t = 2.4$ nm (3 layers). Similarly, ΔP_{max} of 0.03 GPa is obtained for the burst in Fig. S2 with $a = 1.5 \mu m$ and $t = 4.8$ nm (6 layers). On one hand, these values are still about 100 times more than atmospheric pressure. On the other hand, they are at least two orders of magnitude lower than typical tensile strengths of 2D materials and our previously estimated maximum pressure within the bubble. The latter is expected due to an incomplete sub-surface etching and diffusion/escape of the produced gases.

4. Conclusions

In this work, we have addressed the long term structural stability and thermally-induced oxidation of bulk CrSBr crystals in air. The XAS and XPS analyses were performed on fresh and ca. one-year air-exposed CrSBr crystals. Neither fresh nor old samples showed any oxides, but the old samples became contaminated with carbon-based species. Through a careful analysis, we found that prolonged air exposure substantially increased the number of Br vacancies without the change in the number of S vacancies. Furthermore, it also induced defective sulfur and chromium sites. Defective sulfur are probably S atoms bonded to surface adsorbed species, which became possible only after formation of V_{Br} .

Defective Cr has been ascribed to Cr atoms at higher oxidation states than +3.

Next, AFM, XAS and XPS measurements were performed on the CrSBr samples to ponder into any morphological and chemical changes upon their heating. Based on the substantial roughness increase in the AFM topography associated with almost no morphology changes, we proposed that thermal etching of CrSBr had to start with formation of Br vacancies at or below 270 °C. These vacancies increased the surface roughness and opened a possibility for formation of sulfates but yet without any Cr oxides at this temperature, as confirmed by XPS. Heating at 330 °C increased surface roughness even more and induced substantial morphological changes within the sample surface. Such behavior suggested oxidation of elemental Cr and S atoms at this temperature as confirmed by differences in XPS and XAS spectra. In this regard, evolutions of XPS and XAS spectra showed formation of Cr₂O₃ and/or Cr(OH)₃ as well as sulfates. DFT simulations strengthened these conclusions and showed that Br vacancies are more favorable than any other single atoms vacancies such as S and Cr vacancies. The simulations confirmed as well the key role of Br vacancies in further oxidative processes. In particular, the Br vacancies have lowered the activation energy for an initial step of surface oxidation, i.e., dissociative adsorption, from 2.61 eV to 1.54 eV. The former refers to adsorption onto neighboring Cr and S atoms, while the latter to adsorption onto neighboring Cr atoms, one with the Br vacancy.

Thermal oxidation of long-term air-exposed CrSBr crystals resulted in appearance of occasional microscopic bursts of their top-most layers. This is a new phenomenon, related to the sub-surface oxidative etching, which according to our knowledge has not been previously observed in 2D materials. The bursts must have originated from accumulation of gases resulting from oxidative etching of the underlying layers. Applying the membrane theory showed that a determining factor for a bubble rupture was the maximum strain within the CrSBr membrane. Interestingly, the DFT studies showed poisoning of the S vacancies by oxygen atoms and radicals formed after dissociative O₂ splitting. However, they supported favorable oxygen incorporation underneath the top-most layer through the Br vacancies. In such a case an activation energy of 1.64 eV was obtained, which was comparable to oxygen incorporation on the CrSBr surface with Br vacancies as well. The sub-surface oxidative etching produced square-like etch pits due to an orthorhombic crystal lattice of the CrSBr. Such etch pits were not observed on the top-most layer, suggesting some kind of its passivation by surface-bound oxides. Overall, our work confirms that bulk CrSBr crystals are not prone to form oxides but are susceptible to defect formation in ambient conditions.

CRediT authorship contribution statement

Saeed Sovizi: Writing – review & editing, Writing – original draft, Visualization, Validation, Software, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Sergio Tosoni:** Writing – review & editing, Writing – original draft, Visualization, Validation, Software, Methodology, Investigation, Funding acquisition, Formal analysis. **Krzysztof Matlak:** Writing – review & editing, Software, Investigation, Data curation. **Robert Szoszkiewicz:** Writing – review & editing, Writing – original draft, Validation, Supervision, Software, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.flatc.2026.101114>.

Data availability

Data will be made available on request.

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