Novel bismuth oxy hydride chromate (HBi₃(CrO₄)O₃) nano-sheets/rods synthesized by one step one pot wet chemical method

Channegowda Manjunatha
Department of Chemistry, RV College of Engineering, Bengaluru-560059, India
Visvesvaraya Technological University, Belagavi-590018, India
E-mail: manju.chem20@gmail.com and manjunathac@rvce.edu.in

Keywords: inorganic metal hydride, hydrogen bismuth oxy chromate, 2D nanomaterial, bismuth oxy compounds

Abstract
A novel inorganic hydride material, hydrogen bismuth chromium oxide (HBi₃(CrO₄)O₃), with 2D nano sheets and 1D nanorods were prepared for the first time using a simple, green, hazard free hydrothermal method. The X-ray diffraction (XRD) results confirms that the as-formed sample (HBi₃(CrO₄)O₃) has monoclinic crystal system with a space group of P2₁/a. The field emission scanning electron microscope (FESEM) analysis clearly reveal that the new material contains large quantity of 2D nanosheets of thickness <10 nm and spread over >1000 nm and with small amounts of micro-rods of width in the range of 1 to 5 μm and lengths in the range of 40 to 100 μm. The EDS analysis confirms the presence of ‘Bi’, ‘Cr’, and ‘O’ and it further evidences the purity of the sample. The fourier transform infra-red (FT-IR) spectra evidences that the sample has Bi-H, Bi-O and Cr-O bonds as expected for HBi₃(CrO₄)O₃. This material has a potential to find its place in hydrogen storage material, photo/electro catalysis, fuel cells, optoelectronics and rechargeable batteries, therefore it needs materials researcher attention immediately.

1. Introduction
Since last century, the materials scientists have witnessed that the inorganic oxide materials laid foundations for new innovations to technology [1]. Very promisingly, substitution of H⁻ ions into oxides and mixed-anion metallic compounds has gained tremendous attention due to its unique physical and chemical properties [2, 3]. Recent works reported by various researchers reports that inorganic compounds made up off mixed anions, along with oxide ion, like oxhalides and oxyhydrides, offer a superior functionalities [4]. By tuning the structural features of anions such as oxidation state, radii, electronegativity, and polarizability, one can effectively tailor the electronic and structural features. Despite unusual possibilities, the number of compounds containing mixed anions is seldom reported. The bar graph shown in figure 1, clearly displays that the work carried out on mixed anionic compounds are considerably less as compared to single oxide inorganic compounds [5]. The data is recorded from the Inorganic Crystal Structure Database (ICSD) confirms that there are 1266 for oxyfluorides, 612 oxynitrides, 655 oxychalcogenides, 312 oxypnictides and only 47 oxyhydrides. This data clearly tells that the number of oxy-hydride materials discovered are negligible [5].

This new nanomaterial is stoichiometrically similar to Bi₅O₃X, in which X⁻ is replaced by H⁻, and one O²⁻ is replaced by CrO₄²⁻. There are several reports on Bi₅O₃X type of materials, to name a few, photocatalytic Bi₅O₃Cl [6–8], Bi₅O₃Cl/BiOCl [9], superconducting Bi₅O₃S₂Cl [10] etc. However, no nanomaterials of this type have all the three anions such as oxide, hydride, chromate together in the same structure. The material Bi₅O₃X has a layered structure, mostly used in photocatalysis due to its suitable band gap of 2.79 eV [11]. The uniqueness of oxyhydride materials is that they contain hydride (H⁻) ion and also layered structure. Due to its strong reductive nature, with a very high standard redox potential of −2.2 V (H⁻/H₂ versus SHE), it is highly reactive in its ionic form. The major challenges being faced by hydrogen fuel is difficulty in transportation and storage could be solved by using this oxy-hydride hydrogen storage material. Further, this novel oxy-hydride material, provide a new possibilities of handling hydrogen fuel in large scale. There are various metal hydride materials being
reported are considerably different than the mixed anionic hydride compound reported in this work [12–15]. These mixed oxy-hydride compounds are used in battery electrodes, fuel cells, hydrogen storage etc.

The present work reports a method for preparing a hydrogen bismuth chromium oxide (\(\text{HBi}_3(\text{CrO}_4)\text{O}_3\)), a novel inorganic hydride material consisting of nano-sheets and nano-rods for the first time as far as current literature reports are concerned. The experimental procedure proposed for the preparation is very simple, green, hazard free hydrothermal method. The prepared novel material has a large scope for further research on its structural modification, band gap engineering, shapes, and sizes at nanoscale.

2. Experimental

2.1. Chemicals

Bismuth(III) nitrate pentahydrate (99.999% pure), \((\text{Bi(NO}_3)_3 \cdot 5\text{H}_2\text{O}), \text{Mol. Wt. 485.07 g mol}^{-1}\) and Potassium chromate (99.95% pure) \((\text{K}_2\text{CrO}_4), \text{Mol.Wt. 194.19 g mol}^{-1}\) were used as received from Mirck India (Sigma Aldrich) without further purification.
2.2. Characterisation techniques

The crystal structure of the as-formed product was analyzed by using Rigaku SmartLab X-ray diffractometer (XRD). The surface morphology of the product was recorded by FESEM (AMETEK). The FT-IR spectra of the bismuth oxy hydride chromate were recorded using Thermo-Nicolet 6700 FT-IR spectrometer.

Figure 3. SEM images (a to c) and EDX spectra (e) of the as formed HBi$_3$(CrO$_4$)O$_3$. 
2.3. Synthesis of HBi$_3$(CrO$_4$)O$_3$ nano-sheets/rods

In a typical synthesis procedure, stoichiometric amounts of bismuth nitrate (1.455 g) and potassium chromate (0.194 g) salts were dissolved in 80 ml of pure distilled water taken in 100 ml teflon tube. Then the teflon tube was placed in an airtight stainless steel autoclave, followed by hydrothermal heat treatment in hot air oven at 120 °C for 20 h. After the hydrothermal reaction completed, the as-formed product was extracted from the teflon tube, centrifuged, washed and dried.

3. Results and discussion

3.1. XRD results of HBi$_3$(CrO$_4$)O$_3$

The crystalline structure and phase purity of as-synthesized HBi$_3$(CrO$_4$)O$_3$ are determined by XRD analysis. Figure 2 represents the XRD patterns of bismuth oxy hydride chromate (HBi$_3$(CrO$_4$)O$_3$) prepared by hydrothermal method. Almost all the peaks in the XRD spectra can be indexed to standard patterns of hydrogen bismuth chromium oxide JCPDS No 82-1333. It has monoclinic crystal system with a space group of P2$_1$/a, and lattice parameters of $a = 5.527\,\text{Å}$, $b = 12.214\,\text{Å}$, and $c = 14\,\text{Å}$, as per the standard JCPDS data. In addition to the peaks of HBi$_3$(CrO$_4$)O$_3$, there are some noisy peaks due to the presence of negligible amounts of bismuth oxide and chromium oxide, which are possible stable oxides. However, attempts are continued to get 100% pure product, it will be shared in future work.

3.2. FESEM results of HBi$_3$(CrO$_4$)O$_3$

The surface morphology of HBi$_3$(CrO$_4$)O$_3$ was studied by FESEM. Figure 3 represents the FESEM images and EDX spectra of the as-formed sample. The FESEM images clearly reveals that the sample consists of numerous nanosheets with relatively less number of rod shaped structures. From the figure 3(a), it was observed that the sample has micro-rods having width in the range of 1 to 5 $\mu$m and lengths in the range of 40 to 100 $\mu$m. Further, the sample also contains more quantity of nano-sheets as shown in figure 3(b). Figures 3(c) and (d) are the magnified images of figure 3(a), highlighting the presence of 2D nanosheets of thickness <10 nm and spread over >1000 nm. Most of the sheets are partially rolled up and aggregated together. Further, the optimized reaction conditions to achieve the uniform 2D nanosheets will be shared in future work. To check the purity of the sample, EDS analysis was carried out. The EDS spectra shown in figure 3(e) confirm the presence of ‘Bi’, ‘Cr’, ‘O’ elements. However, the ‘H’ element can’t be recorded in EDS technique, as it is related to the K-shells valence electrons and ‘H’ element does not have ‘K’ valence shell. The absence of other elements confirms the purity of the sample. Further, the presence of ‘H’ can be confirmed by FT-IR spectra shown in figure 4.

3.3. FT-IR spectral studies of HBi$_3$(CrO$_4$)O$_3$

FT-IR spectroscopy is a very potential tool, extensively used to identify both organic, and inorganic compounds. It provides the information on the presence of various possible bonding types, which helps in understanding the structural features and also the purity of materials. Figure 4 represents the FT-IR spectra of the as-formed HBi$_3$(CrO$_4$)O$_3$. The presence of 3452 cm$^{-1}$ band corresponding to −(OH) groups stretching vibration, confirms

Figure 4. FTIR spectra of the as formed HBi$_3$(CrO$_4$)O$_3$. 

4
the presence of the coordinated water molecules groups originating from chemisorbed and non-dissociated water molecules on the surface of the sample. Generally M-H (metal hydride) is reported to show bending modes only around 1000–1300 cm\(^{-1}\) and stretching modes around 1600 cm\(^{-1}\). The stretching and bending modes with respect to HBi\(_3\)(CrO\(_4\))O\(_3\) metal hydride are in good agreement with the results described for various other metal hydrides [16, 17]. The peak around 845 cm\(^{-1}\) is attributed to Cr–O bond of CrO\(_4\) tetrahedra [18, 19]. The sharp peak at 800 cm\(^{-1}\) and 500 cm\(^{-1}\) represents the presence of Bi–O bond [20]. It is more often reported that the M–H–M bonds are typically found in the region from 800 to 1600 cm\(^{-1}\). Therefore, the IR band corresponding to metal hydride (M–H) can be seen at 1348 cm\(^{-1}\), which further evidences the formation of metal hydride [21]. Generally, for terminal metal-hydrogen stretching bands, the FT-IR peaks appear between 2100 and 1700 cm\(^{-1}\) and for bridging M–H–M bands are found at relatively lower frequencies (1700–1000 cm\(^{-1}\)) [21]. These observation clearly confirms the Bi–H, Bi–O, Cr–O bonds and supporting the existence of HBi\(_3\)(CrO\(_4\))O\(_3\).

4. Conclusion

In summary, 2D nanosheets of a novel metal hydride HBi\(_3\)(CrO\(_4\))O\(_3\) was prepared by one pot one step, simple and green hydrothermal method for the first time. The XRD results confirm the formation of monoclinic HBi\(_3\)(CrO\(_4\))O\(_3\) and FESEM results clearly demonstrate the formation of 2D nanosheets of thickness <10 nm and spread over >1000 nm and micro-rods with width in the range of 1 to 5 μm and lengths in the range of 40 to 100 μm. The EDS analysis confirms the presence of Bi, Cr, O and also the purity of the sample. Further, FT-IR spectral results support the formation of this new compound. This new 2D nanomaterial would be the potential candidate for inorganic materials researchers, nanomaterials scientists to explore more possibilities in their structural features like bonding, layered crystal structure, and very importantly to explore its application in hydrogen fuel storage, battery, photo/electro catalyst applications.

Acknowledgments

Author is grateful to the Management RSST trust, and principal of RV College of Engineering, Bengaluru, INDIA for their constant support and encouragement.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

ORCID iDs

Channegowda Manjunatha @ https://orcid.org/0000-0003-0422-9614

References

[1] Tabor D P, Roch I M, Saikin S K, Kreisbeck C, Sheberla D, Montoya J H, Dwaraknath S, Aykol M, Ortiz C and Tribukait H 2018 Accelerating the discovery of materials for clean energy in the era of smart automation Nature Reviews Materials 3 5–20
[2] Hanna T, Muruba Y, Matsuishi S, Igawa N, Kodama K, Shimoto K, Hoseno H 2011 Hydrogen in layered iron arsenides: Indirect electron doping to induce superconductivity Physical Review B 84 024521
[3] Hayward M, Cussen E, Claridge J, Bieringer M, Bosseinsky M, Kielc B, Blundell S, Marshall I and Pratt F 2002 The hydride anion in an extended transition metal oxide array: LaSrCeO3H0.7 Science 295 1882–4
[4] Takei F, Watanae A, Kuwabara A, Nawaz H, Aya N I P, Yonemura M, Kanno R and Kobayashi G 2019 Ba2ScH3O3: H− conductive layered oxyhydride with H−site selectivity Inorg. Chem. 58 4431–6
[5] Kageyama H, Hayashi K, Maeda K, Attfield J P, Hiroi Z, Rondinelli J M and Poeppelmeier K R 2018 Expanding frontiers in materials chemistry and physics with multiple anions Nat. Commun. 9 772
[6] Xu B, Gao Y, Li Y, Liu S, Lv D, Zhao S, Gao H, Yang G, Li N and Ge L 2020 Synthesis of Bi3O4Cl nanosheets with oxygen vacancies: The effect of defect states on photocatalytic performance Appl. Surf. Sci. 507 144806
[7] Ning S, Shi X, Zhang H, Lin H, Zhang Z, Long J, Li Y and Wang X 2019 Reconstructing dual-induced [0 0 1] facets bismuth oxychloride nanosheets heterostructures: an effective strategy to promote photocatalytic oxygen evolution Sol. RRL 3 1900059
[8] Li J, Zhang L, Li Y and Yu Y 2014 Synthesis and internal electric field dependent photoreactivity of Bi 3 O 4 Cl single-crystalline nanosheets with high [001] facet exposure percentages Nanoscale 6 167–71
[9] Ning S, Ding L, Lin Z, Lin Q, Zhang H, Lin H, Long J and Wang X 2016 One-pot fabrication of Bi3O4Cl/BiOCl plate–on–plate heterojunction with enhanced visible-light photocatalytic activity Appl. Catalysis B 185 203–12
[10] Ruan B-B, Zhao K, Mu Q-G, Fan B-J, Liu T, Yang H-X, Li J-Q, Chen G-F and Ren Z-A 2019 Superconductivity in Bi3O2S2Cl with Bi–Cl Planar Layers JACS 141 3404–8
[11] Lin X, Huang T, Huang F, Wang W and Shi J 2006 Photocatalytic activity of a Bi-based oxychloride Bi3O4Cl. J. Phys. Chem. B 110 24629–34

[12] Bridges C A, Darling G R, Hayward M A and Rosseinsky M J 2005 Electronic structure, magnetic ordering, and formation pathway of the transition metal oxide hydride LaSrCoO3H0.7 JACS 127 5996–6011

[13] Yamamoto T, Zeng D, Kawakami T, Arcisaukaite V, Yata K, Patino M A, Izumo N, McGrady J E, Kageyama H and Hayward M A 2017 The role of π-blocking hydride ligands in a pressure-induced insulator–to–metal phase transition in SrVO2H Nat. Commun. 8 1–7

[14] Kobayashi Y, Hernandez O J, Sakaguchi T, Yajima T, Rossne T, Tsujimoto Y, Morita M, Noda Y, Mogami Y and Kitada A 2012 An oxyhydride of BaTiO3 exhibiting hydride exchange and electronic conductivity Nat. Mater. 11 507–11

[15] Tassel C, Goto Y, Kuno Y, Hester J, Green M, Kobayashi Y and Kageyama H 2014 Direct synthesis of chromium perovskite oxyhydride with a high magnetic-transition temperature Angew. Chem. 126 10545–8

[16] Javadian P, GharibDoust S P, Li H-W, Sheppard D A, Buckley C E and Jensen T R 2017 Reversibility of LiBH4 facilitated by the LiBH4–Ca (BH4)2 eutectic The Journal of Physical Chemistry C 121 18439–49

[17] Mészáros L S, Ceccaldi P, Lorenzi M, Redman H J, Pfützner E, Heberle J, Senger M, Stripp S T and Berggren G 2020 Spectroscopic investigations under whole-cell conditions provide new insight into the metal hydride chemistry of [FeFe]-hydrogenase Chem. Sci. 11 4608–17

[18] Mehraj O, Sofi F A, Moosvi S K, Naqash W and Majid K 2018 Synthesis of novel silver chromate incorporated copper–metal-organic framework composites with exceptionally high photocatalytic activity and stability J. Mater. Sci., Mater. Electron. 29 3358–69

[19] Güy N and Özacar M 2019 Ag/Ag2CrO4 nanoparticles modified on ZnO nanorods as an efficient plasmonic photocatalyst under visible light J. Photochem. Photobiol., A 370 1–11

[20] Seddigi Z S, Gondal M A, Baig U, Ahmed S A, Abdulaziz M, Danish E Y, Khaled M M and Lais A 2017 Facile synthesis of light harvesting semiconductor bismuth oxychloride nano photo-catalysts for efficient removal of hazardous organic pollutants PLoS One 12 e0172218

[21] D’Anna V, Spyratou A, Sharma M and Hagemann H 2014 FT-IR spectra of inorganic borohydrides Spectrochim. Acta, Part A 128 902–6