Review Study of Some Sillen Structure Chloride Phosphor Materials

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Abstract

Silicates and halides have long been recognized as effective luminescent materials, each with distinct advantages and disadvantages. Silicates are stable but require higher synthesis temperatures, while halides are more suitable for applications like optically stimulated luminescence and scintillation due to their lower melting points and the importance of defects and colour centres. However, most halides, except for fluorides, are quite hygroscopic, which can affect their stability in ambient conditions and necessitate protective measures. Sillen structure lattices present a promising alternative, as they can be synthesized at significantly lower temperatures than silicates and are less hygroscopic than their halide counterparts. Despite their potential, research on sillen structure has not been as extensive as that on silicates and halides. This review aims to summarize existing studies on the synthesis, crystal structures, and luminescence of various Sillen structure chloride phases, encouraging further research in this area.

Keywords: Silicates, Halides, Sillen structure chloride, Synthesis, Crystal structures & Luminescence.
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Introduction

Halides are extremely effective luminous materials that are commonly employed in optically stimulated luminescence (OSL), thermoluminescence (TL), and scintillation due to their ability to generate defects, colour centres, and excitons. Halides have a low melting point, which provides advantages; nonetheless, their hygroscopic nature, with the exception of fluorides, necessitates preventive measures for stability under ambient settings [1].

Chloride-based phosphors, which are a subgroup of halides, are gaining popularity due to their distinct optical features and versatility. They have uses in lighting, high-performance displays, radiation detection (for example, PET scans), dosimetry, and sophisticated technologies like quantum dots and nanophotonics. Their low synthesis temperatures enable devices that are both energy efficient and sustainable. However, their hygroscopic nature restricts their use in humid situations, prompting further study to increase stability and widen applications [1-3].

Sillen bismuth-based oxyhalides, first reported in 1941 [1], are renowned for their catalytic characteristics [2, 3, 11, 12], unusual crystal structures [13-18], and Bi^{3+} luminescence [4-10]. Compounds like $SrBiO_2Cl$, $BaBiO_2Cl$, and $CaBiO_2Cl$ display photoluminescence and radioluminescence, making them suitable for advanced applications. The Sillen X1 series ($ABi^{3+}O_2X$; A = Cd, Ca, Sr, Ba, Pb; X = Cl, Br, I) has three primary crystallographic forms: tetragonal (I4/mmm), orthorhombic (Cmcm), and monoclinic (P21/m) [19], making it valuable for efficient and creative luminous materials.

Sillen structures have various advantages, although they have not been investigated as thoroughly as silicates and halides. This lack of research has left gap in our understanding of their synthesis methods, crystal structures, and luminous characteristics. This review examines current knowledge on Sillen structure chloride phases, with a focus on their synthesis, crystal characteristics, and luminous activity. By summarizing these findings, the study aims to highlight the unexplored potential of these materials and

Table 1: Summarizes typical synthesis and Characterization for various Bismuth Oxychloride.

Parameters	$BaBiO_2Cl$	$CaBiO_2Cl$	$SrBiO_2Cl$
Synthesis Method	$BaCO_3$+BiOCl, 700-800°C	Varying reactants calcination 600-800°C	$SrCO_3$+BiOCl, 700-800°C
Crystal Structure	Orthorhombic (Cmcm)	Monoclinic ($P2_1/m$)	Orthorhombic (Cmcm)
Doping Effects	Maintains phase purity	Lattice distortion with Ag, Co, Ni doping	Bi^{3+} active in photocatalysis
Bandgap	2.53 eV-3.71 eV	2.5 eV – 3.4 eV	2.88 eV – 3.52 eV
Photocatalytic Activity	Enhanced by Doping	Improved with metal doping	Superior dye degradation, better charge separation
PL Characteristics	Strong emission, red up conversion (doped), reduced at high Temperature	Blue shift with calcination temperature	Blue shifted emission, stable luminescence.

stimulate future research to widen their applications in advanced luminous technologies.

Materials and Methods: Bismuth Based Oxyhalides

1. Barium Bismuth Oxychloride ($BaBiO_2Cl$)

Several researchers studied $BaBiO_2Cl$ using solid-state methods, commonly heating $BaCO_3$ and BiOCl at temperatures ranging from 700-800 °C [20-25]. X-ray diffraction (XRD) investigation indicated that the compound had an orthorhombic structure with the Cmcm space group, and doping was discovered to maintain phase purity [21, 23, 25]. SEM images show that pure $BaBiO_2Cl$ is made up of layer-stacked nanoplates, while doped samples have more irregular morphologies [21, 23]. Optical studies revealed bandgaps ranging from 2.53 eV to 3.71 eV, with doping improving light absorption and photocatalytic activity [21–25]. Photoluminescence (PL) studies revealed strong emissions and red upconversion luminescence in doped samples, while the intensity reduced with increasing temperature [20, 23, 24]. These findings demonstrate the potential of $BaBiO_2Cl$ for photo catalytic and luminescent applications.

2. Calcium Bismuth Oxychloride ($CaBiO_2Cl$)

Several researchers studied of $CaBiO_2Cl$ using multiple solid-state techniques, employing different reactants and calcination conditions [20, 22, 26, 29]. X-ray diffraction (XRD) study confirmed its monoclinic structure ($P2_1/m$). Doping with Ag, Co, and Ni caused lattice aberrations and enhanced light absorption. FESEM and SEM showed plate-like morphologies in pure $CaBiO_2Cl$, whereas doped samples had lower particle sizes [27-28]. Optical evaluation with UV-Vis DRS and FTIR revealed lower bandgaps ranging from 2.5 to 3.4 eV, resulting in increased photocatalytic performance, particularly in metal-doped samples under visible light [26–28]. Photoluminescence investigations revealed blue shift in emission spectra as calcination temperatures increased [26]. These findings emphasize the tunable photocatalytic capabilities of $CaBiO_2Cl$, particularly when doped with metals.

3. Strontium Bismuth Oxychloride ($SrBiO_2Cl$)

Several researchers studied of $SrBiO_2Cl$ utilizing several solid-state techniques and conditions [21-22, 24, 29, 30]. Characterization studies revealed an orthorhombic structure (Cmcm space group) with high crystallinity and no detected impurities [20-30]. The Rietveld refinement analysis revealed a layered structure comprised of alternating $[SrBiO_2]^+$ and Cl^- layers, with Bi^{3+} ions playing a substantial role in photocatalytic activity [20-22, 29-30]. SEM and FESEM images revealed a layered nanoplate morphology [21]. Optical studies using UV-Vis DRS revealed bandgaps ranging from 2.88 to 3.52 eV, allowing for photocatalysis driven by both UV and visible light. The photoluminescence investigation revealed blue-shifted emission, reduced charge recombination, and steady luminescence [20-21, 24, 30]. Photocatalytic tests showed that $SrBiO_2Cl$ is more effective than $BaBiO_2Cl$ for dye degradation due to better charge separation and enhanced hydroxyl radical production [21-22, 30]. These findings emphasize $SrBiO_2Cl$'s potential for enhanced photocatalytic and optoelectronic applications [20, 24].

Conclusion

$BaBiO_2Cl$, $CaBiO_2Cl$, and $SrBiO_2Cl$ are promising compounds for photocatalysis and luminescence applications, each with its own advantages and limitations. $BaBiO_2Cl$ has stable photocatalytic activity under UV light for organic pollutant degradation and strong luminescent characteristics, with potential applications in anti-counterfeiting, bioimaging, and photodynamic treatment. $CaBiO_2Cl$'s photocatalytic effectiveness is boosted via structural changes and doping techniques, resulting in improved pollutant degradation and light absorption. $SrBiO_2Cl$'s improved hydroxyl radical production enhances photocatalytic performance under UV light and demonstrates promising luminous capabilities for light-emitting devices.

Together, these compounds provide a broad platform for environmental remediation, innovative materials, and energy applications. Future study on $BaBiO_2Cl$, $CaBiO_2Cl$, and $SrBiO_2Cl$ should focus on enhanced doping methods, hybrid structures, and composites to improve photocatalytic efficiency, light absorption, and charge separation. Furthermore, research into their potential applications in environmental remediation, optoelectronics, energy harvesting, and sustainable luminous devices is critical for large-scale, multifunctional utilization.

References

1. Sharma, K., & Moharil, S. V. (2023), *"Review of chlorosilicates as phosphor hosts"*, Crystal Research and Technology, 58(1), 2200272. https://doi.org/10.1002/crat.202200272.
2. Sillen, L. G. (1941), Rontgenuntersuchung von Calcium/Wismutoxychloriden und -oxybromiden. Zeitschrift für anorganische und allgemeine Chemie, 248(1), 121. https://doi.org/10.1002/zaac.19412480203.
3. Thomas, J. M., Ueda, W., Williams, J., & Harris, K. D. M. (1989), *"New families of catalysts for the selective oxidation of methane"*, Faraday Discussions of the Chemical Society, 87, 33. https://doi.org/10.1039/DC9898700033.
4. Burch, R., Chalker, S., Loader, P., Thomas, J. M., & Ueda, W. (1992), *"Investigation of ethene selectivity in the methane coupling reaction on chlorine-containing catalysts"*, Applied Catalysis A: General, 82(1), 77–90, https://doi.org/10.1016/0926-860X(92)80185-9.
5. Blasse, G., & Bril, A. (1968), *"Investigations on Bi^{3+}-activated phosphors"*, The Journal of Chemical Physics, 48(1), 217–222, https://doi.org/10.1063/1.1667890.
6. Dieguez, E., Arizmendi, L., & Cabrera, J. M. (1985), *"X-ray induced luminescence, photoluminescence, and thermoluminescence of $Bi_4Ge_3O_{12}$"*, Journal of Physics C: Solid State Physics, 18(24), 4777–4786. https://doi.org/10.1088/0022-3719/18/24/021.
7. Jacquier, B., Boulon, G., Sallavuard, G., & Gaume-Mahn, F. (1972), *"Bi^{3+} center in a lanthanum gallate phosphor"*, Journal of Solid-State Chemistry, 4(3), 374–378. https://doi.org/10.1016/0022-4596(72)90152-1.
8. Kim, C.-H., Pyun, C.-H., Choi, H., & Kim, S.-J. (1999). *"Luminescence of CaS:Bi"*, Bulletin of the Korean Chemical Society, 20(3), 337–340, https://doi.org/10.5012/bkcs.1999.20.3.337.
9. Moncorgé, R., Jacquier, B., & Boulon, G. (1976), *"Temperature dependent luminescence of $Bi_4Ge_3O_{12}$: Discussion of possible models"*, Journal of Luminescence, 14(5–6), 337–348. https://doi.org/10.1016/0022-2313(76)90003-X.
10. Shionoya, S., & Yen, W. M. (2000), *"The phosphor handbook (Vol. 1)"*, CRC Press. https://doi.org/10.1201/9781420041552.
11. Weber, M. J., & Monchamp, R. R. (1973), *"Luminescence of $Bi_4Ge_3O_{12}$: Spectral and decay properties"*, Journal of Applied Physics, 44(12), 5495–5499. https://doi.org/10.1063/1.1662183.
12. Burch, R., Chalker, S., Loader, P. K., Thomas, J. M., & Ueda, W. (1992), *"Investigation of ethene selectivity in the methane coupling reaction on chlorine-containing catalysts"*, Applied Catalysis A: General, 82(1), 77–90, https://doi.org/10.1016/0926-860X(92)80156-8.
13. Thomas, J. M., Ueda, W., Williams, J., & Harris, K. D. M. (1989), *"New families of catalysts for the selective oxidation of methane"*, Faraday Discussions of the Chemical Society, 87, 33–48. https://doi.org/10.1039/DC9898700033.
14. Charkin, D. O., Berdonosov, P. S., Dolgikh, V. A., & Lightfoot, P. (2003), *"A reinvestigation of quaternary layered bismuth oxyhalides of the Sillen X1 type"*, Journal of Solid-State Chemistry, 175(2), 316–321. https://doi.org/10.1016/S0022-4596(03)00297-4.
15. Dolgikh, V. A., & Kholodkovskaya, L. N. (1992), *"The crystal chemistry of layer metal oxide halides and oxide chalcogenides (Sillén phases)"*, Russian Journal of Inorganic Chemistry, 37(5), 488–496.
16. Fray, S. M., Milne, C. J., & Lightfoot, P. (1997). *"Synthesis and structure of $CaBiO_2Cl$ and $SrBiO_2Cl$: New distorted variants of the Sillén X1 structure"*, Journal of Solid-State Chemistry, 129(1), 115–120, https://doi.org/10.1006/jssc.1996.7245.
17. Kennard, M. A., Darriet, J., Grannec, J., & Tressaud, A. (1995), *"Cation ordering in the Sillén X1-type oxychloride, $BaBiO_2Cl$"*, Journal of Solid-State Chemistry, 117(1), 201–205, https://doi.org/10.1006/jssc.1995.1263.
18. Sillen, L. G. (1939), *"Uber die Struktur der Oxyhalogenide des dreiwertigen Bismuts"*, Zeitschrift für anorganische und allgemeine Chemie, 242(1), 41–62, https://doi.org/10.1002/zaac.19392420105.
19. Sillen, L. G. (1942), *"Uber die Kristallstruktur von BiOCl"*, Naturwissenschaften, 22(15), 318–319. *https://doi.org/10.1007/BF01475647*.
20. Olchowka, J., Kabbour, H., Colmont, M., Adlung, M., Wickleder, C., & Mentre, O. (2016), *"$ABiO_2X$ (A = Cd, Ca, Sr, Ba, Pb; X = Halogen) Sillen X1 series: Polymorphism versus optical properties"*, Inorganic Chemistry, 55(14), 7009–7018. https://doi.org/10.1021/acs.inorgchem.6b01024.
21. Huang, H., Wang, S., Zhang, Y., & Han, X. (2015), *"$MBiO_2Cl$ (M = Sr, Ba) as novel photocatalysts: Synthesis, optical property, and photocatalytic*

activity", Materials Research Bulletin, 62, 206–211. https://doi.org/10.1016/j.materresbull.2014.11.032.

22. Lin, X.-P., Huang, F.-Q., Wang, W.-D., Shan, Z.-C., & Shi, J.-L. (2008), *"A series of Bi-based oxychlorides as efficient photocatalysts"*, Key Engineering Materials, 368–372, 1503–1506. https://doi.org/10.4028/www.scientific.net/KEM.368-372.1503.
23. Zhang, Z., & Liang, Y. (2022), *"Synthesis and upconversion luminescence properties of $BaBiO_2Cl:Yb^{3+}$, Er^{3+} phosphor"*, Crystals, 12(10), 1465. https://doi.org/10.3390/cryst12101465.
24. Porter-Chapman, Y., Bourret-Courchesne, E., & Derenzo, S. E. (2008), "Bi^{3+} luminescence in $ABiO_2Cl$ (A = Sr, Ba) and $BaBiO_2Br$", Journal of Luminescence, 128, 87–91, https://doi.org/10.1016/j.jlumin.2007.05.007.
25. Peng, J., Peng, Y., Wang, T., Wu, Z., Wang, Q., Li, Y., Yin, Z., Han, J., Qiu, J., Yang, Z., & Song, Z. (2022), *"Enhanced UV–Vis–NIR photocatalytic activity of La-doped $BaBiO_2Cl$: Role of oxygen vacancies"*, Journal of Solid-State Chemistry, 314, 123381, https://doi.org/10.1016/j.jssc.2022.123381.
26. Shi, R., Xu, T., Zhu, Y., & Zhou, J. (2012), *"High photocatalytic activity of oxychloride $CaBiO_2Cl$ under visible light irradiation"*, CrystEngComm, 14, 6257–6263, https://doi.org/10.1039/c2ce25672j.
27. Feng, Y., Huang, W., Hu, C., Zhao, W., Jiao, P., Zhong, Y., & Zhou, H. (2014), *"Preparation of Ag-modified $CaBiO_2Cl$ and its photocatalytic ability under visible light"*, Advanced Materials Research, 955–959, 120–126. https://doi.org/10.4028/www.scientific.net/AMR.955-959.120.
28. Zhu, B.-Q., Hu, C.-H., Feng, Y., Yin, X.-H., Zhong, Y., & Zhou, H.-Y. (2015), *"Synthesis and photocatalytic activity of M-doped $CaBiO_2Cl$ (M = Ag, Co, and Ni) under visible light"*, ICMSA 2015 Conference Proceedings, https://doi.org/10.2991/icmsa-15.2015.118.
29. Fray, S. M., Milne, C. J., & Lightfoot, P. (1997), *"Synthesis and structure of $CaBiO_2Cl$ and $SrBiO_2Cl$: New distorted variants of the Sillén X1 structure"*, Journal of Solid-State Chemistry, 128, 115–120, https://doi.org/10.1006/jssc.1996.7229.
30. Suzuki, H., Kunioku, H., Higashi, M., Tomita, O., Kato, D., Kageyama, H., & Abe, R. (2018), *"Photocatalytic water oxidation by a Sillén-related oxychloride $PbBiO_2Cl$"*, Chemistry of Materials, 30, 5862–5869, https://doi.org/10.1039/d3ta00906h.