

New Hybrid Halogenobismuthates as Candidates for Non-linear Optical Properties

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Non-linear optical materials play an important role in the field of laser technology, as they allow for the changing of a laser beam's properties. One example of a non-linear optical property which a material may have is second harmonic generation, which causes the frequency of a passing through laser beam to double. In order for a material to possess the ability to generate a second harmonic frequency, certain criteria for the crystal structure must be met, most notably it must be acentric. Herein, we report several novel hybrid halogenobismuthates, specifically chlorobismuthates and iodobismuthates, which were synthesized and characterized in order to find possible acentric candidates for use as non-linear optical materials. These compounds were found using two approaches to finding acentric crystal structures.

First, organic cations from previously synthesized lead bromide compounds were used, as these lead bromide compounds crystallized in acentric space groups. [1] Using this approach, three compounds were found, which crystallized in acentric space groups and contained either dimethylpyridinium (DMP) or 3-iodopropylammonium (3-IPA) cations, namely monoclinic (*Cc*) (DMP)BiCl₄, orthorhombic (*P2₁2₁2₁*) (DMP)₃Bi₂I₉ and orthorhombic (*Pna2₁*) (3-IPA)₃BiI₆. In (DMP)BiCl₄, Bi³⁺ is octahedrally coordinated by Cl. These octahedra form *cis*-chains via edge-sharing (see figure 1). The nitrogen atoms of the DMP-cations are all orientated in the same direction in the *a,b*-plane, resulting in the acentric space group. In (DMP)₃Bi₂I₉, Bi³⁺ and I form dimers of face-sharing BiI₆ octahedra, resulting in Bi₂I₉ units. (3-IPA)₃BiI₆ contains isolated BiI₆ octahedra.

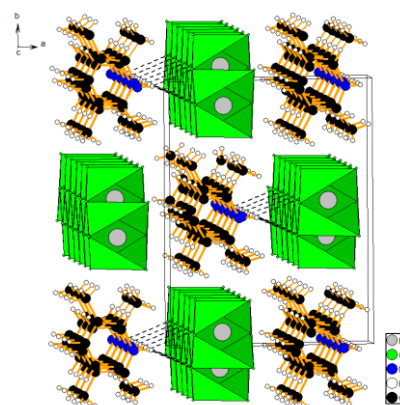


Fig 1: Unit cell of (DMP)BiCl₄

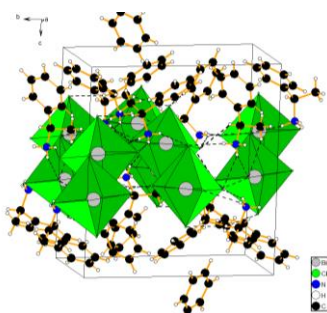


Fig 2: Unit cell of (R-1-PEA)₂BiCl₅

Second, chiral organic cations were employed in order to induce an acentric symmetry, known from the chiral templating technique. [2] This resulted in four non-centrosymmetric compounds which contain 1-phenethylammonium (1-PEA) in either R or S configuration, namely monoclinic (*P2₁*) (R-1-PEA)₂BiCl₅, (S-1-PEA)₂BiCl₅, (R-1-PEA)₂BiI₅ and (S-1-PEA)₂BiI₅. These compounds crystallize isotypic, though the R and S structures are mirror images of one another. Here, Bi³⁺ is octahedrally coordinated by Cl or I. Two such octahedra form edge-sharing Bi₂X₁₀ (X = Cl, I) units (see figure 2).

[1] M. Krummer. Dissertation, Albert-Ludwigs-Universität Freiburg, not yet published.

[2] K.-z. Du, Q. Tu, X. Zhang, Q. Han, J. Liu, S. Zauscher, and D. B. Mitzi, *Inorg. Chem.* **56**(15), 2017, 9291