A tetragonal tungsten bronze with extremely large second harmonic generation intensity

Yunseung Kuk and Kang Min Ok*

Department of Chemistry, Sogang University, 35 Baekbeom-ro, Mapo-gu, Seoul 04107, Republic of Korea
kmok@sogang.ac.kr

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Solid-state materials with macroscopic noncentrosymmetric (NCS) structures have been widely studied for their interesting properties, including ferroelectricity, piezoelectricity, pyroelectricity, and nonlinear optical (NLO) properties [1-3]. Tungsten bronze with polar structures, such as Pb₂K₀.₅Li₀.₅Nb₅O₁₅ (Cm2m; 30 × KH₂PO₄ (KDP)), Pb₂(Pb₀.₁₅Li₀.₇⁵□₀.₁₅)Nb₅O₁₅ (Pn₂₁m; 39 × KDP; □: vacancies), and Pb₂.₁₅(Li₀.₂₅Na₀.⁷⁵)₀.⁷Nb₅O₁₅ (Bb₂₁m; 47 × KDP), have been shown to exhibit strong second harmonic generation (SHG) responses [4, 5]. However, it is worth noting that these materials have mainly been studied as ferroelectric materials, despite their potential as NLO materials. In this study, we successfully synthesized a tetragonal tungsten bronze by combining second-order Jahn-Teller distortive cations through a solid-state reaction. The crystal structure of the title compound was determined by single crystal X-ray diffraction and Rietveld refinement, which reveal that the title compound crystalized in the NCS space group, P4bm (No. 100), composed of the three-dimensional (3D) framework with NbO₆, PbO₁₂, and Pb/KO₁₅ polyhedra (Fig. 1). Remarkably, the title compound exhibits an extremely large SHG efficiency of about 71.5 times that of KDP, as well as a type-I phase-matching behavior. To the best of our knowledge, the title compound exhibits the strongest SHG efficiency among the reported NLO materials to date. In this presentation, synthesis, crystal growth, structure, and characterization of a new tetragonal tungsten bronze are presented along with the detailed calculations such as magnitude of octahedral distortions and net dipole moments to explain the observed very strong SHG response.

Figure 1. The crystal structure of the title compound with tetragonal tungsten bronze-type frameworks by corner-sharing NbO₆ octahedra.

Reference

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