Wide-spectrum NLO materials obtained by polycation-substitution-induced NLO-functional motif ordering

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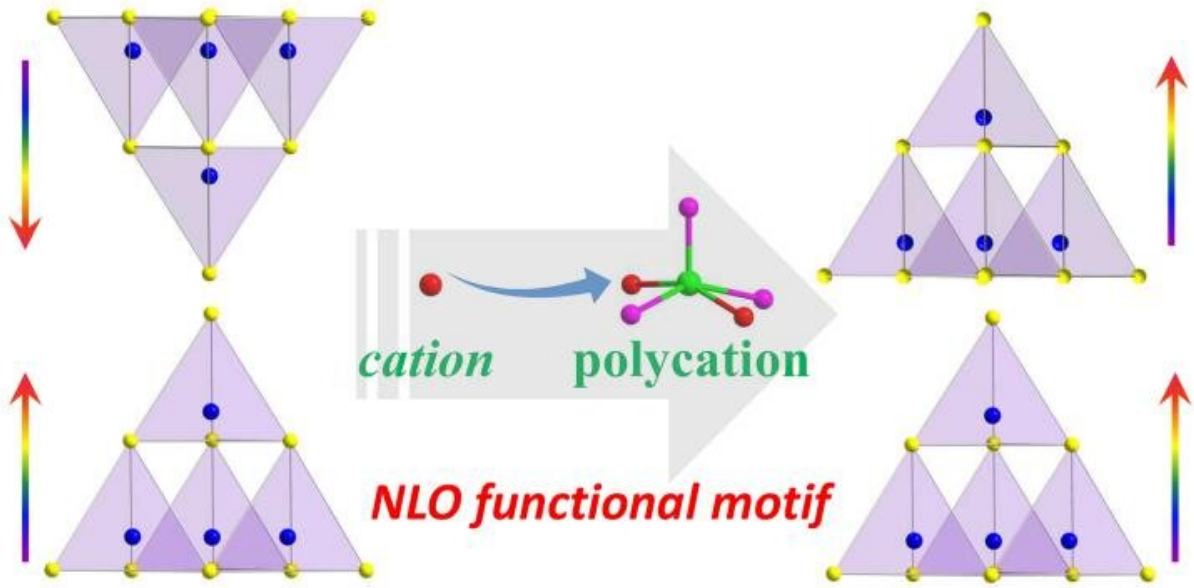

Schematic illustration of reconstructing NLO-functional motif in a parallel fashion via polycation-substitution-induced CS-to-NCS transformation strategy. Credit: Prof. GUO's group

Nonlinear optical (NLO) crystals possess a frequency conversion capability that is significant for national defense and civil applications. Noncentrosymmetry (NCS) is a prerequisite for second-order NLO materials, but designing NCS structures is a challenging task.

In a study published in the *Journal of the American Chemical Society*, a group led by Prof. Guo Guocong at Fujian Institute of Research on the Structure of Matter (FJIRSM) of the Chinese Academy of Sciences, reported two novel NCS salt-inclusion chalcogenides: ABa_2Cl and Ga_4S_8 (A = Rb, Cs), which are the first examples achieved through polycation-substitution-induced centrosymmetry (CS)-to-NCS transformation and NLO-functional motif ordering.

The researchers constructed the $[Ga_4S_8]_4$- layers in $RbGaS_2$ by apex-sharing T2-supertetrahedra Ga_4S_{10}. Although the $[Ga_4S_8]_4$ unit is NLO-active, $RbGaS_2$ cannot produce second harmonic generation (SHG) efficiency because the neighboring $[Ga_4S_8]_4$ layers in its structure stack in a back-to-back style, which results in a CS space group of C2/c and cancels out their hyperpolarizabilities.

Therefore, the researchers succeeded in replacing the Rb+ in $RbGaS_2$ with acentric polycation $[ClA_2Ba_3]_7^+$ via the salt-inclusion synthesis method, affording two new NCS sulfides, $[ABa_2Cl][Ga_4S_8]$ (A = Rb, Cs).

They discovered that the orderly arrangement of NLO-active T2-supertetrahedral Ga_4S_{10} motifs resulting from the template effect of polycation $[ClA_2Ba_3]_7^+$ is responsible for the remarkable SHG intensities (10.4–15.3× KH_2PO_4 (KDP) at 1064 nm; 0.9–1.0×$AgGaS_2$ at 1910 nm).

Those experimental results, together with high laser-induced damage thresholds (11–12×$AgGaS_2$), wide transparent window (0.4-12.3 μm), and phase-matchable behavior, indicate that $[ABa_2Cl][Ga_4S_8]$ (A = Rb, Cs) are promising wide-spectrum NLO materials used in both Vis and IR regions.

This study provides an effective approach for designing new NLO materials.

More information: Bin-Wen Liu et al. $[ABa_2Cl][Ga_4S_8]$ (A = Rb, Cs): Wide-Spectrum Nonlinear Optical Materials Obtained by Polycation-Substitution-Induced Nonlinear Optical (NLO)-Functional Motif Ordering, *Journal of the American Chemical Society* (2020). DOI: 10.1021/jacs.0c04738

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