Researchers develop nonlinear optical crystals by unusual cationic substitution strategy

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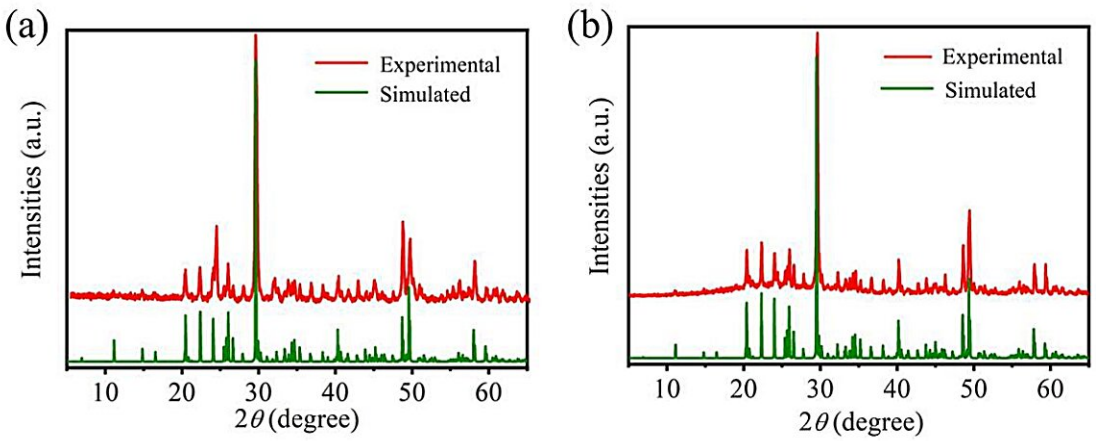

Powder XRD patterns of 1 (a) and 2 (b). Credit: *Small* (2023). DOI: 10.1002/smll.202305711

An ideal infrared (IR) nonlinear optical (NLO) crystal must have the advantages of a wide transmittance range, impressive laser-induced damage threshold (LIDT), sufficient birefringence index, bulk single-crystal form, and physicochemical stability.

However, there is often a trade-off between a strong NLO coefficient and a wide band gap toward high LIDT, making it challenging to achieve both properties in a single material.

Recently, a research group led by Prof. Guo Guocong from the Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, reported two novel non-centrosymmetric chalcogenides: $M[M_4Cl][Ga_{11}S_{20}]$ (M = A/Ba, A = K, Rb) as excellent nonlinear optical crystals.

The study was published in *Small* on Sept. 11.

$M[M_4Cl][Ga_{11}S_{20}]$ (M = A/Ba, A = K, Rb) represent the first examples achieved by a cationic substitution strategy, resulting in salt-inclusion chalcogenides with diamond-like anionic frameworks.

The researchers used to consider typical diamond-like chalcogenides as promising candidates for IR NLO materials; however, they often exhibit limited LIDTs due to their narrow band gaps.

In this study, the researchers employed an unconventional cationic substitution strategy, $[[SZn_4]S_{12} + [S_4Zn_{13}]S_{24} + 11ZnS_4 => MS_{12} + [M_4Cl]S_{24} + 11GaS_4]$, to create two novel salt-inclusion sulfides, $M[M_4Cl][Ga_{11}S_{20}]$ (M = A/Ba, A = K, Rb). As anticipated, the introduction of mixed cations in the GaS_4 anionic frameworks resulted in wide band gaps (3.04 and 3.01 eV) and improved high LIDTs (9.4 and 10.3 × $AgGaS_2$@1.06 μm).

Furthermore, the researchers found that the ordered arrangement of tetrahedral GaS_4 units favored strong second-harmonic generation intensities (0.84 and 0.78 × $AgGaS_2$@2.9 μm).

This study is an example of employing a cationic substitution strategy based on diamond-like structures to create high-performance NLO materials.

More information: Xiao-Yu Lou et al, Excellent Nonlinear Optical

M[M4Cl][Ga11S20] (M = A/Ba, A = K, Rb) Achieved by Unusual Cationic Substitution Strategy, *Small* (2023). DOI: 10.1002/smll.202305711