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Heteroanion-introduction-driven birefringence enhancement in oxychalcogenide $Ba_3M^{II}Ge_3O_2S_8$ ($M^{II} = Mn, Cd$)†

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Birefringent crystals play a crucial role in regulating the polarization of light and are widely used in optoelectronic fields. However, the effective design of novel infrared (IR) birefringent crystals with large birefringence (Δn) still face significant challenges. In this study, we present the rational design and successful synthesis of two novel quinary oxychalcogenides with the formula $Ba_3M^{II}Ge_3O_2S_8$ ($M^{II}=Mn$, Cd), employing a heteroanion-introduction strategy via high-temperature solid-state reactions. $Ba_3M^{II}Ge_3O_2S_8$ ($M^{II}=$ Mn, Cd) crystallized in the monoclinic space group $P2_1/n$ (no. 14) and the structures comprised onedimensional (1D) $[M^{II}Ge_3S_8O_2]^{6-}$ chains arranged in an antiparallel manner and separated by Ba^{2+} cations. The coexistence of multiple heteroanionic ligands ($[M^{II}OS_{5}]$ octahedra, $[GeOS_{5}]$, and $[GeO_{2}S_{2}]$ tetrahedra) in one material was surprisingly discovered for the first time in the realm of oxychalcogenides. It was revealed that the heteroanion-introduction strategy not only leads to a reduction in the structural dimensionality but also enhances the optical anisotropy significantly. Notably, $Ba_3M^{II}Ge_3O_2S_8$ ($M^{II}=Mn$, Cd) demonstrated large Δn values of 0.11 and 0.14, which represent a remarkable improvement compared to the three-dimensional (3D) parent $AE_3M^{\parallel}M_2^{\parallel}Q_8$ system ($\Delta n=0$). Furthermore, theoretical calculations suggest that the significant Δn of Ba₃M^{II}Ge₃O₂S₈ (M^{II} = Mn, Cd) resulted primarily from the combination of polarizabilities from the various heteroanionic groups. Overall, these results highlight the potential of the heteroanion-introduction strategy for designing novel IR birefringent materials for optoelectronic applications.

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1. Introduction

Birefringent crystals play a crucial role in high-performance optics, especially in polarization apparatus, phase-matching elements, and laser processing. Currently, the majority of the commercially available birefringent crystals are inorganic oxides, such as YVO_4 , $CaCO_3$, and α -BaB₂O₄. However, these materials have their limitations. For instance, they suffer from detrimental metal-oxygen (M-O) bond absorptions, which

restrict their usage in the infrared (IR) region. Conversely, the current commercially available birefringent crystals are suitable for the ultraviolet and visible region, and few birefringent crystals has been explored for the IR region. In addition, the excellent birefringence (Δn) of crystals enables the downsizing of crystal optical devices.⁵ Consequently, there is an increasing demand for high-performance IR birefringent crystals in both the scientific research and technological development fields.

The analysis of the structure–property relationships of birefringent crystals revealed a positive correlation between the Δn and anisotropy.⁶ In other words, a larger anisotropy corresponds to a greater Δn . Effective structural design strategies can be employed to modulate the Δn , such as introducing π -conjugated units,⁷ stereochemically active lone pairs (SCALPs),⁸ and functional building units (FBUs) with large polarizability anisotropy.⁹ Recently, the heteroanion-introduction strategy has been proved to be an effective and direct approach for boosting the Δn , such as Rb₂VO(O₂)₂F ($\Delta n = 0.189$ @ 546 nm),¹⁰ Sn₂BO₃I ($\Delta n = 0.393$ @ 546 nm), Sn₂PO₄I ($\Delta n = 0.664$ @ 546 nm),¹¹ RbTeMo₂O₈F ($\Delta n = 0.263$ @ 546 nm),¹² and K₂Sb(P₂O₇)F ($\Delta n = 0.157$ @ 546 nm).¹³

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Oxychalcogenides with rich structures, varying from isolated zero-dimensional (0D) to dense three-dimensional (3D) frameworks, are an exciting class of heteroanionic system that have attracted significant attention in recent years owing to their high Δn , which can obtained by partial anion substitution from the parent structure.¹⁴ Some examples include Ba₃Ge₂O₄Te₃ (0.14 @ 2090 nm, maternal structure: Ba₂ZnGe₂O₇), ¹⁵ SrGeOSe₂ (0.16 @ 2050 nm, maternal structure: SrGeO₃), ¹⁶ Sr₂CdGe₂OS₆ (0.193 @ 2050 nm, maternal structure: $Sr_2CdGe_2O_7$, ¹⁷ $Nd_3[Ga_3O_3S_3][Ge_2O_7]$ (0.091 @) 2050 nm, maternal structure: $Cs_3[Sb_3O_6][Ge_2O_7]$, and Sr₂ZnSn₂OS₆ (0.12 @ 2050 nm, maternal structure: Sr₂ZnSi₂O₇).¹⁹ The parent structures mentioned above are all oxides. However, no examples have been reported using chalcogenides as parent structures to generate new oxychalcogenides by introducing oxygen atoms.

The quaternary $AE_3M^{II}M_2^{IV}Q_8$ (AE = Sr, Ba; M^{II} = divalent transition metals; M^{IV} = Ge, Sn; Q = chalcogen) family is a complex system that distinguishes itself as an intriguing nonlinear optical (NLO) system owing to its structural flexibility at every crystallographic site.²⁰ However, its crystallization in the cubic space group results in the Δn values of 0, rendering it incapable of achieving phase-matching in NLO applications. Inspired by the previous strategy of introducing heteroanions, we successfully obtained two new oxychalcogenides, i.e. $Ba_3M^{II}Ge_3O_2S_8$ ($M^{II} = Mn$, Cd). In this study, the syntheses, structures, optical properties, and birefringent characteristics of the title compounds are described. Furthermore, theoretical calculations were conducted to achieve a better understanding of the structure-activity relationships.

2. Results and discussion

In the structure of AE₃M^{II}M₂^{IV}Q₈, the [M^{IV}Q₄] tetrahedron links $3 [M^{II}Q_4]$ tetrahedra while $[M^{II}Q_4]$ links $4 [M^{IV}Q_4]$ tetrahedra to build up a 3D framework. Inside this framework, chargebalanced AE²⁺ cations are located in the cavity (Fig. 1a and c). Unfortunately, the dense 3D structure, which crystallizes in the cubic system (space group $I\bar{4}3d$ (no. 220)), has an inappropriate anisotropy, resulting in a Δn value of 0 for $AE_3M^{II}M_2^{IV}Q_8$, and thereby rendering phase-matching impossible. It is widely recognized that the anisotropic polarization of a structure significantly impacts its Δn . Hence, the search for low-dimensional structures exhibiting significant anisotropy is considered one of the most effective means to obtain materials with a large Δn .²¹

The oxychalcogenides Ba₃M^{II}Ge₃O₂S₈ (M^{II} = Mn, Cd) represent a novel type of quinary compound discovered in AE/MII/ M^{IV}/Q/O systems. These compounds crystallize in the centrosymmetric monoclinic space group $P2_1/n$ (no. 14); their detailed crystallographic information is shown in Table 1. The asymmetric unit consists of three independent Ba sites, one independent MII site, three independent Ge sites, two independent O sites, and eight independent S sites. All the independent atom sites are located in the Wyckoff position 4e. The

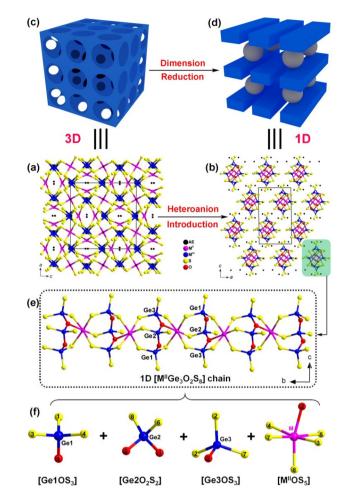


Fig. 1 Structural evolution from 3D AE₃M^{II}M₂^{IV}Q₈ to 1D Ba₃M^{II}Ge₃O₂S₈: (a and b) ball-and-stick models viewed from the ac-plane; (c and d) schematic diagram of equivalent models; (e) projection of the 1D $[MGe_3O_2S_8]^{6-}$ chain along the *bc*-plane; (f) coordination environment of [GeOS₃], [GeO₂S₂], and [M^{II} OS₅] (M^{II} = Mn, Cd) FBUs with the atom numbers marked.

basic structure of Ba₃M^{II}Ge₃O₂S₈ can be seen as composed of 1D [M^{II}Ge₃O₂S₈]⁶⁻ infinite chains, while AE²⁺ cations fill the space to balance the charge (refer to Fig. 1b and d). The coordination environments of Ge and MII atoms are shown in Fig. 1f, and the key bond distances and angles are given in Table S1.† Ge1 and Ge3 atoms are linked to 1 O atom and 3 S atoms, forming heteroanionic [GeOS₃] FBUs with Ge-S bond lengths in the regular range of 2.174-2.205 Å and Ge-O bond distances of 1.806-1.838 Å. The Ge2 atom, on the other hand, is linked to 2 O atoms and 2 S atoms, forming heteroanionic [GeO₂S₂] FBUs with Ge-S bond lengths in the range of 2.137-2.178 Å and Ge-O bond lengths in the range of 1.779–1.787 Å. The M^{II} atom is coordinated with 1 O and 5 S atoms to form a highly distorted [MIOS5] octahedron, with MII-S and MII-O bond lengths falling within the normal ranges.²² Two [GeOS₃] FBUs and one [GeO₂S₂] FBU form a [Ge₃O₂S₈] cluster through bridging O atoms. These clusters are then interconnected with octahedral [M^{II}OS₅] FBUs, resulting

Table 1 Crystal data structural refinement details $Ba_3M^{II}Ge_3O_2S_8$ ($M^{II} = Mn, Cd$)

Inorganic Chemistry Frontiers

Empirical formula	Ba ₃ CdGe ₃ O ₂ S ₈	Ba ₃ MnGe ₃ O ₂ S ₈
CCDC	2234469	2234468
Formula weight	1030.67	973.21
Temperature (K)	293(2)	293(2)
Crystal system	Monoclinic	Monoclinic
Crystal color	Light yellow	Light yellow
Size (mm ³)	$0.08 \times 0.10 \times$	$0.07 \times 0.10 \times$
	0.10	0.11
Space group	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)
a (Å)	8.8294(10)	8.8298(7)
$b(\mathring{A})$	11.9334(13)	11.8254(11)
$c(\mathbf{\hat{A}})$	15.2993(17)	15.2442(11)
β (°)	90.839(2)	90.548(7)
$V(A^3)$	1611.8(3)	1591.7(2)
Z	4	4
$D_{\rm c} ({\rm g cm}^{-3})$	4.247	4.061
$\mu (\mathrm{mm}^{-1})$	15.037	14.684
GOOF on F^2	1.139	1.119
R_1 , w $R_2 (I > 2\sigma(I))^a$	0.0265, 0.0720	0.0456, 0.1248
R_1 , w R_2 (all data)	0.0290, 0.0725	0.0483, 0.1233
Largest diff. peak and hole (e \mathring{A}^{-3})	1.512, -1.727	2.520, -1.257

 ${}^{a}R_{1} = \sum ||F_{0}| - |F_{c}||/\sum |F_{0}|, wR_{2} = [\sum w(F_{0}^{2} - F_{c}^{2})^{2}/\sum w(F_{0}^{2})^{2}]^{1/2}.$

in the formation of 1D [MIGe₃O₂S₈]⁶⁻ infinite chains through face-sharing (Fig. 1e). The Ba atoms also have different coordination behaviors. For instance, Ba1 and Ba3 atoms are surrounded by 8 S atoms, forming a [BaS₈] bicapped trigonal prism. On the other hand, the Ba2 atom is surrounded by 1 O atom and 7 S atoms, resulting in a more twisted [BaOS₇] bicapped trigonal prism (Fig. S1 and S2†).

The detailed structural evolution from 3D AE₃M^{II}M₂^{IV}Q₈ to 1D Ba₃M^{II}Ge₃O₂S₈ is depicted in Fig. 1. The introduction of O atoms, which have a different electronegativity ($\chi_{\rm O}$ = 3.44 vs. $\chi_{\rm S}$ = 2.58), can be viewed as acting like structural scissors to break the dense high-dimensional framework structure, resulting in the formation of a loosely connected low-dimensional chain structure. Consequently, a significantly anisotropic structure was obtained. This could be further confirmed by the experimental results and theoretical research on birefringence discussed in the following section.

Furthermore, through comparing and analyzing the reported oxychalcogenides, we discovered that Ba₃M^{II}Ge₃O₂S₈ (M^{II} = Mn, Cd) demonstrated structural novelty in three distinct aspects. First, the heteroanionic [GeO_xQ_{4-x}] FBUs can only exist in a singular form in oxychalcogenides, 23-28 such as $[GeO_2S_2],$ and [GeO₃Se], identified AE₃Ge₂O₄Te₃, ^{15,23} AEGeOS₂, ²⁵ and Sr₃Ge₂O₄Se₃, ²⁷ respectively. However, the title compounds simultaneously contained two $[GeO_xS_{4-x}]$ FBUs, namely, $[GeOS_3]$ and $[GeO_2S_2]$. Second, it has been reported that there are relatively few oxychalcogenides with transition-metal-based [TMO_xQ_v] FBUs, ²⁹ but some examples include $[ZnO_2S_2]$ in BaZnOS, 30 $[ZnOS_3]$ in SrZn₂S₂O,³¹ [CoO₂S₂] in BaCoOS,³² and [CoOS₃] in CaCoOS.³³ Notably, in contrast to the previously reported four-coordinated [TMO_xQ_y], two new heteroanionic FBUs, [MnOS₅] and [CdOS₅], were successfully observed in Ba₃M^{II}Ge₃O₂S₈ (M^{II}

= Mn, Cd) for the first time, which enhances the diversity of oxychalcogenides. Third, compounds with two or more heteroanionic FBUs are currently very rare, with the few examples limited to $Ba_6V_4O_5S_{11}$ ([VOS₃] + [VO₂S₂])³⁴ and (Ba₁₉Cl₄) $(Ga_6Si_{12}O_{42}S_8)$ ($[GaOS_3] + [GaO_2S_2]$).³⁵ The coexistence of multiple heteroanionic FBUs (octahedral [MIOS₅], tetrahedral [GeOS₃] and [GeO₂S₂]) in the title compounds was surprisingly discovered for the first time in the realm of oxychalcogenides.

The compounds Ba₃M^{II}Ge₃O₂S₈ (M^{II} = Mn, Cd) were synthesized using a traditional high-temperature solid-state method. Single crystals with a millimeter-size were carefully selected for characterization and measurement (Fig. 2). The elemental analysis of Ba₃M^{II}Ge₃O₂S₈ (M^{II} = Mn, Cd) confirmed the symmetrical distribution through EDX mapping, and the Ba: M^{II}: Ge: O: S ratio was found to be highly consistent with the results obtained from single-crystal XRD (Fig. S3 and S4†). The purity phase of Ba₃M^{II}Ge₃O₂S₈ (M^{II} = Mn, Cd) was examined by powder XRD measurements (see Fig. 2a and b). The experimental results matched well with the simulated patterns derived from the single-crystal XRD measurements. The UV-Vis-NIR diffuse reflectance spectrum revealed optical energy gap (E_g) values of 3.82 and 3.39 eV for Ba₃CdGe₃O₂S₈ and Ba₃MnGe₃O₂S₈ (Fig. 2c and d), respectively, using the Kubelka-Munk function.³⁶ These values are higher compared to other reported TM-based oxychalcogenides, such as $Sr_6Cd_2Sb_6O_7S_{10}$ (1.89 eV),³⁷ $Sm_3NbS_3O_4$ (2.68 eV),³⁸ and $[Sr_3VO_4][InSe_3]$ (2.62 eV).³⁹ Additionally, $Ba_3M^{II}Ge_3S_8O_2$ (M^{II} = Mn, Cd) exhibited high thermal stability up to 1100 K under a N₂ atmosphere based on the thermal analysis (Fig. S5†). There were no melting or phase transition behaviors observed in the corresponding DSC curves, which was consistent with the powder XRD results (Fig. S6†). Furthermore, Ba₃CdGe₃O₂S₈ (MII = Mn, Cd) demonstrated a broad IR transmission cut-off

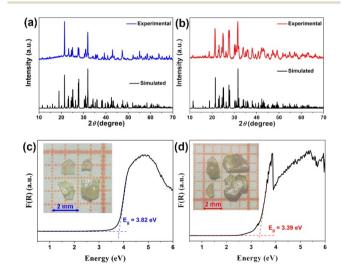


Fig. 2 Characterization of $Ba_3M^{II}Ge_3O_2S_8$ ($M^{II}=Mn$, Cd): experimental and simulated powder XRD patterns for the as-synthesized (a) $Ba_3CdGe_3S_8O_2$ and (b) $Ba_3MnGe_3S_8O_2$; optical E_q for (c) $Ba_3CdGe_3S_8O_2$ and (d) Ba₃MnGe₃S₈O₂ (inset: optical images of the target single crystals).

region from 2.5 to 13.3 µm (Fig. S7†), indicating their potential as IR birefringent candidates.

Inspired by oxychalcogenides that exhibit an appropriate Δn value, ⁴⁰ the Δn of Ba₃CdGe₃O₂S₈ (M^{II} = Mn, Cd) was also measured using a ZEISS Axio A1 cross-polarizing microscope. The retardations (R values) and crystal thicknesses (T values) were tested as 1.073 μm and 9.8 μm for $Ba_3MnGe_3O_2S_8,$ and 0.85 μm and 5.9 μm for Ba₃CdGe₃O₂S₈ respectively. Notably, the measured Δn values for Ba₃MnGe₃O₂S₈ and Ba₃CdGe₃O₂S₈ were found to be 0.11 and 0.14, respectively, using the formula $\Delta n = R/T$ (Fig. 3).⁴¹ These values are larger than those of commercial materials like MgF₂ (0.012 @ 632 nm)⁴² and LiNbO₃ (0.08 @ 632 nm),43 as well as many recently reported chalcogenides, such as $[Ba_4(S_2)][ZnGa_4S_{10}]$ (0.053 @ 1064 nm),⁴⁴ LiBaSbS $_3$ (0.045 at 532 nm), 45 and $K_2Na_2Sn_3S_8$ (0.070 at 546 nm).46 This indicates that the target compounds have potential as birefringent materials. Moreover, it is noteworthy that compared to the 3D $AE_3M^{II}M_2^{IV}Q_8$ with a Δn value of 0, the 1D Ba₃M^{II}Ge₃O₂S₈ (M^{II} = Mn, Cd) oxychalcogenides displayed appropriate Δn values. These findings indicate that the heteroanion-introduction strategy is effective in increasing optical anisotropy and boosting Δn in the oxychalcogenide family.

For a more comprehensive understanding of the electronic structures and optical performances of Ba₃M^{II}Ge₃O₂S₈ (M^{II} = Mn, Cd), detailed theoretical calculations were conducted using the DFT method. As depicted in Fig. S8† and Fig. 4a, Ba₃MnGe₃O₂S₈ and Ba₃CdGe₃O₂S₈ exhibited direct band gaps, with calculated $E_{\rm g}$ values of 1.53 and 2.47 eV, respectively. These values were notably different from the tested values obtained from the UV-vis-NIR spectra (3.39 and 3.82 eV). This

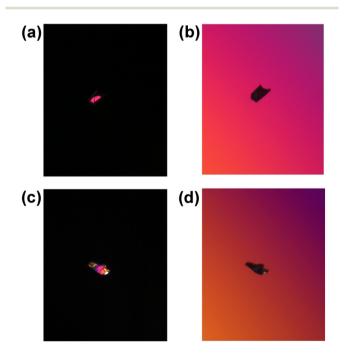


Fig. 3 (a and b) $Ba_3MnGe_3O_2S_8$ and (c and d) $Ba_3CdGe_3O_2S_8$ crystals for birefringence determination and the interference colors observed before and after complete extinction.

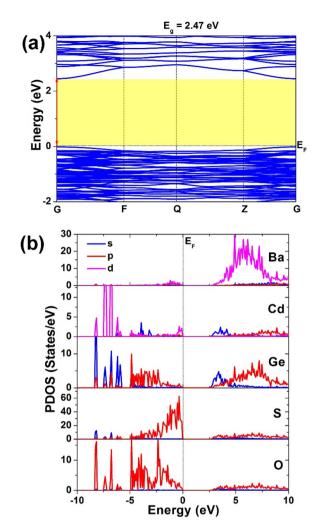
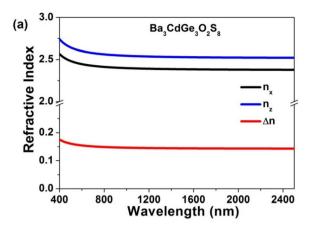


Fig. 4 Theoretical calculated results of Ba₃CdGe₃O₂S₈: (a) electronic band structure; (b) PDOS curve.

discrepancy may be attributed to the limited accuracy of the conventional DFT functional in describing band gaps. 47 A detailed Brillouin zone plot with high symmetry points is provided in Fig. S9.† Since the Ba₃MnGe₃O₂S₈ and Ba₃CdGe₃O₂S₈ compounds demonstrated similarities in the partial density of states (PDOS) curves (Fig. 4b and S8†), Ba₃CdGe₃O₂S₈ was chosen as the representative compound for further elucidation. In the PDOS graphs, the valence band maximum (VBM) was defined by the S-3p and O-2p nonbonding states, while the conduction band minimum (CBM) was dominated by the unoccupied Cd-4s, Ge-3s, and Ba-4p orbitals. Thus, the E_g of Ba₃CdGe₃O₂S₈ was primarily determined by the heteroanionic [GeOS₃], [GeOS₃] and [CdOS₅] FBUs, namely, 1D [CdGe₃O₂S₈]⁶⁻ chains.

Besides, based on DFT calculations, the Δn of $Ba_3M^{II}Ge_3O_2S_8$ (M^{II} = Mn, Cd) was also calculated (Fig. 5a and S10†). The results reveal that the calculated Δn of Ba₃CdGe₃O₂S₈ was 0.15 @ 2050 nm. Additionally, when combined with the analysis by the partial charge density graphs in the VBM and CBM ranges (Fig. 5b), it was evident that the het-



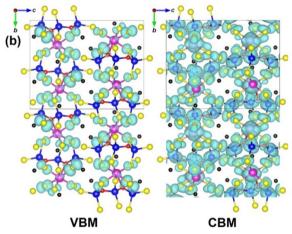


Fig. 5 (a) Calculated refractive index dispersion curves and birefringence of Ba₃CdGe₃O₂S₈; (b) distribution of the partial charge density maps in the VBM and CBM parts. Black atoms: Ba; pink atoms: Cd; blue atoms: Ge; yellow atoms: S; red atoms: O.

eroanionic FBUs play a significant role in achieving a large Δn . This implies that the introduction of heteroanions into the structure is favorable to the structural anisotropy.

3. Conclusions

With the aim of obtaining new IR birefringent materials in the AE-TM-M^{IV}-O-Q system, two novel oxychalcogenides Ba₃M^{II}Ge₃O₂S₈ (M^{II} = Mn or Cd) were successfully synthesized by employing a heteroanion-introduction strategy of replacing part of the Q atoms from the parent AE₃M^{II}M₂^{IV}Q₈. This is the first case that contains multiple heteroanionic ligands in oxychalcogenides, and the 1D anionic [MIGe₃O₂S₈]⁶⁻ chain is exclusively constructed by three heteroanionic units, that is, octahedral [M^{II}OS₅], and tetrahedral [GeOS₃] and [GeO₂S₂]. Both compounds exhibited a large $E_{\rm g}$ (3.39 and 3.82 eV), a broad IR transparency region (2.5-13.3 µm), and good thermal stability (approximately 1100 K). Specifically, Ba₃M^{II}Ge₃O₂S₈ $(M^{II} = Mn \text{ or } Cd)$ demonstrated a large Δn (0.11 and 0.14 @ 549 nm), implying its potential application as an IR birefringent candidate. Analysis of their structure-property relationships displayed that the 1D chains in a reversed arrangement is favorable for generating a large Δn . Overall, this study represents significant progress in the field of IR birefringent materials and presents a new paradigm for developing crystal structures with enhanced Δn that are suitable for optoelectronic applications.

Author contributions

Sheng-Hua Zhou: investigation, methodology, validation, writing - original draft. Mao-Yin Ran: investigation, formal analysis, writing - original draft. Wen-Bo Wei: formal analysis, validation. A-Yang Wang: formal analysis, validation. Xin-Tao Wu: conceptualization, writing - review & editing. Hua Lin: supervision, conceptualization, writing - review & editing. Qi-Long Zhu: supervision, writing - review & editing.

Conflicts of interest

There are no conflicts to declare.

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