Supporting information

Hydrothermal growths, optical features and first-principles calculations of sillonite-type crystals comprising discrete \( \text{MO}_4 \) tetrahedra

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Fig. S1 Powder X-ray diffraction patterns of \( M \)-doped \( \alpha \)-Bi\(_2\)O\(_3\) crystals (\( M \) = Zn, P, Ni, La, Cd, Cr, Al) by mild hydrothermal methods.
**Fig. S2** Unit cell parameters and volumes as a function of the composition of Bi$_{12}$(Bi$_{1-x}$Fe$_x$)O$_{20}$.

**Fig. S3-S8** Rietveld refinement plot of the powder X-ray diffraction profile of Bi$_{12}$(Bi$_x$M$_{1-x}$)O$_{20}$ ($M = $ V, Fe, Ga, Ge, Mn, P).

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\text{Bi}_{12}\text{(Bi}_{0.195}\text{V}_{0.805})\text{O}_{20}
\]

- Space group: \(I\ 23\)
- \(a = b = c = 10.2339(1)\ \text{Å}\)
- \(V = 1071.81(3)\ \text{Å}^3\)
- \(R_{wp} = 8.91\)
- \(R_p = 6.74\)
Bi$_{12}$(Bi$_{0.498}$Fe$_{0.502}$)O$_{20}$

Space group: $I\ 2\ 3$

$a = b = c = 10.1650(1)\ \text{Å}$

$V = 1050.31(3)\ \text{Å}^3$

$R_{wp} = 11.53$

$R_p = 8.22$

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Bi$_{25}$GaO$_{40}$

Space group: $I\ 2\ 3$

$a = b = c = 10.1716(1)\ \text{Å}$

$V = 1052.36(2)\ \text{Å}^3$

$R_{wp} = 7.66$

$R_p = 5.76$
Bi$_{12}$GeO$_{20}$

Space group: $I23$

$a = b = c = 10.1441(1)$ Å

$V = 1043.85(2)$ Å$^3$

$R_{wp} = 10.89$

$R_p = 7.94$

Bi$_{12}$(Bi$_{0.375}$Mn$_{0.625}$)O$_{20}$

Space group: $I23$

$a = b = c = 10.2153(1)$ Å

$V = 1066.00(3)$ Å$^3$

$R_{wp} = 8.99$

$R_p = 6.53$
Fig. S9 IR absorbance spectrum of the as-grown Bi$_{12}$(Bi$_{0.375}$Mn$_{0.625}$)O$_{20}$ crystal.
**Fig. S10** XPS pattern of the as-grown $\text{Bi}_{12}(\text{Bi}_{0.375}\text{Mn}_{0.625})\text{O}_{20}$ crystal.

**Fig. S11** PDOS projected on each species of atoms in $\text{Bi}_{12}\text{SiO}_{20}$. The straight dashed line indicates the VBM.
Fig. S12 PDOS projected on each species of atoms in Bi$_{25}$FeO$_{40}$.

Fig. S13 PDOS projected on each species of atoms in Bi$_{25}$MnO$_{40}$.