Supporting Information:

Understanding the Interactions between Vibrational Modes and Excited State Relaxation in $Y_{3-x}Ce_xAl_5O_{12}$: Design Principles for Phosphors Based on $5d$–$4f$ Transitions

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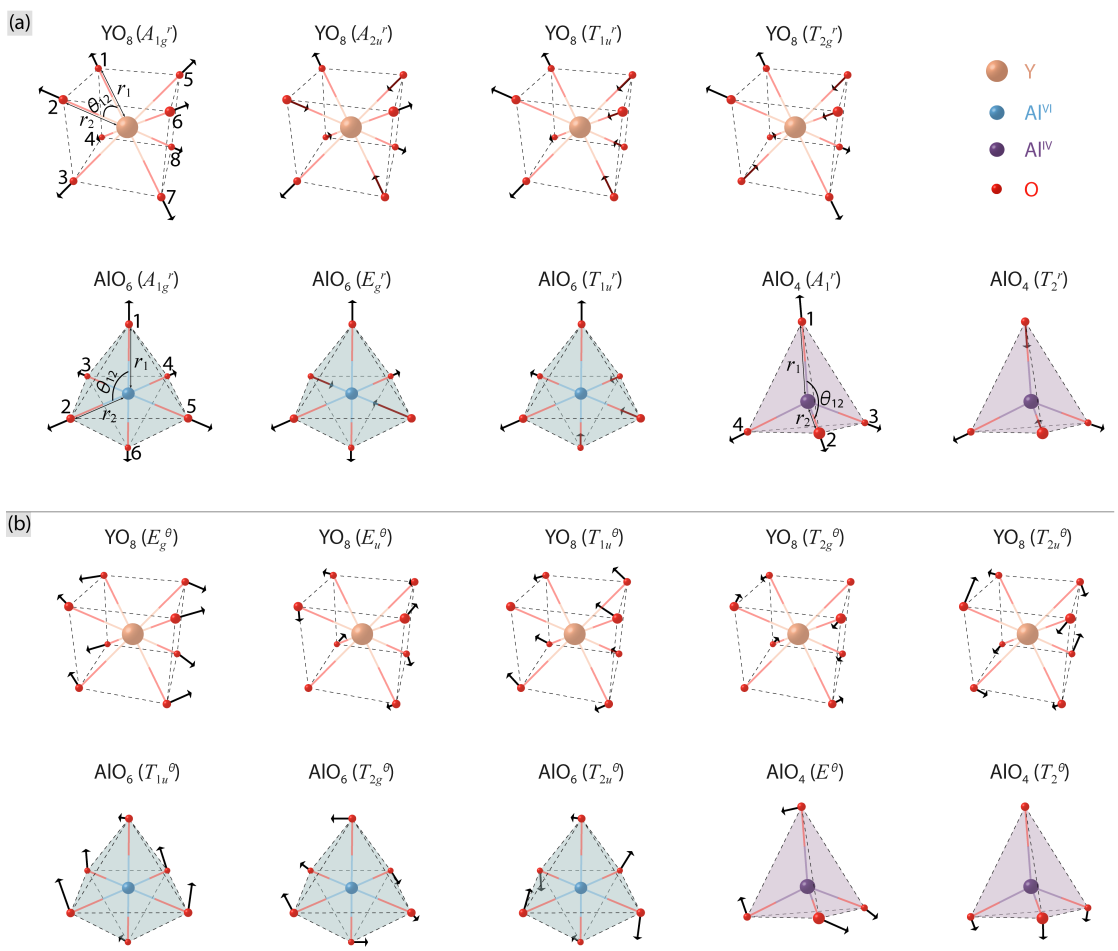

Figure S1 Symmetry coordinates, $|\eta\rangle$, for (a) stretching and (b) bending vibrations of cubic YO_8, octahedral AlO_6, and tetrahedral AlO_4 moieties. See Table S1 for mathematical expression of the symmetry coordinates.

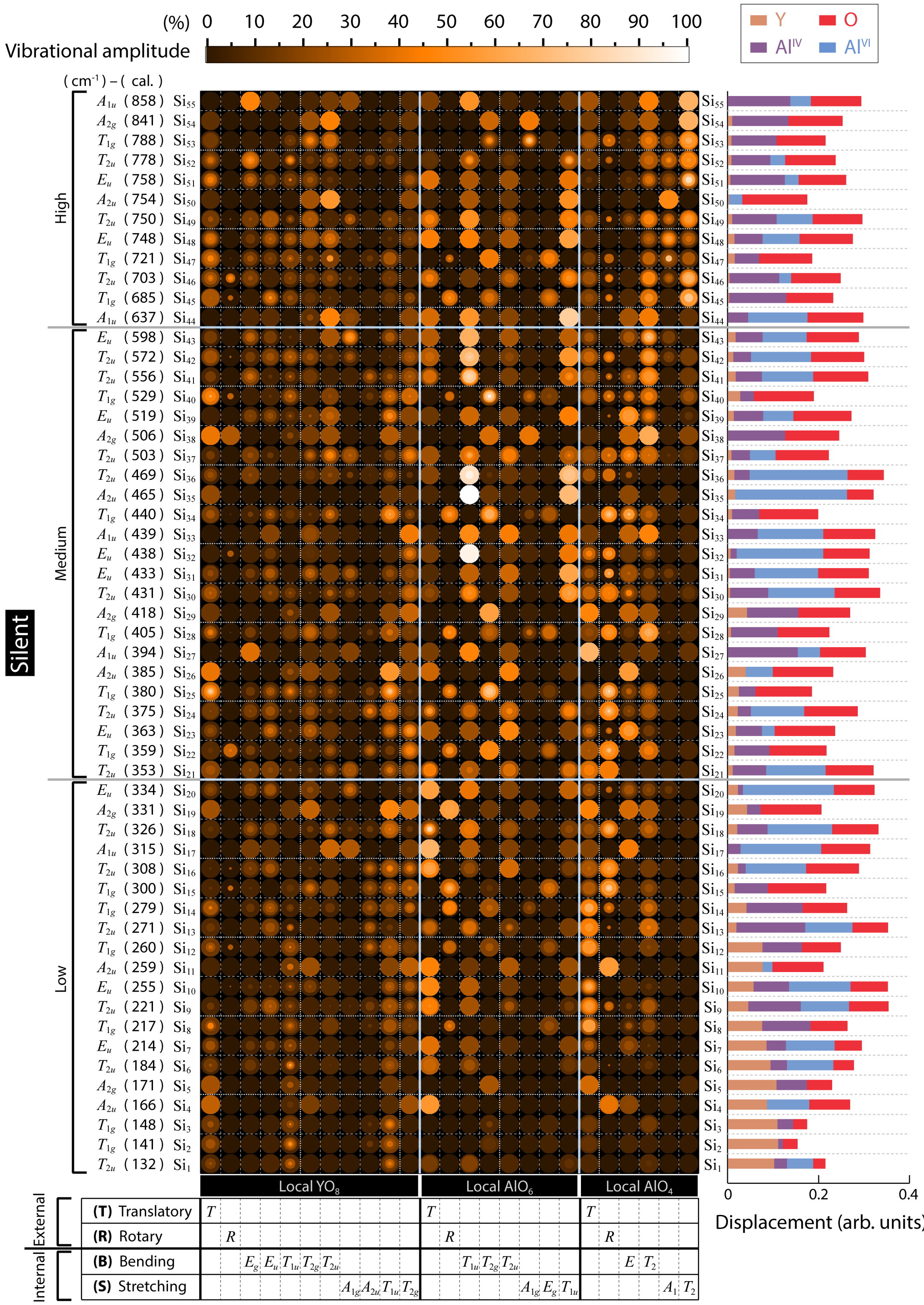

Figure S2 *Left:* full PDM for silent normal modes of YAG. *Right:* average atomic displacements of Y, Al^{VI}, Al^{IV}, and O atoms.

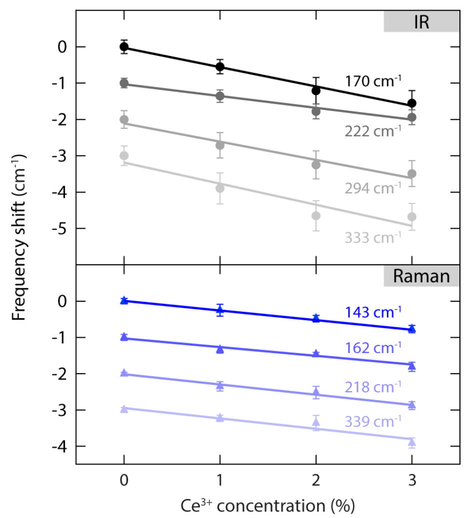

Figure S3 Vibrational frequency shift of YAG:z%Ce^{3+} upon increasing Ce^{3+} dopant concentration from $z = 0$ to $z = 3$. IR-active modes at 222, 294, and 333 cm^{-1} are offset by -1, -2, and -3 cm^{-1}, respectively. Raman-active modes at 162, 218, and 339 cm^{-1} are offset by -1, -2, and -3 cm^{-1}, respectively.

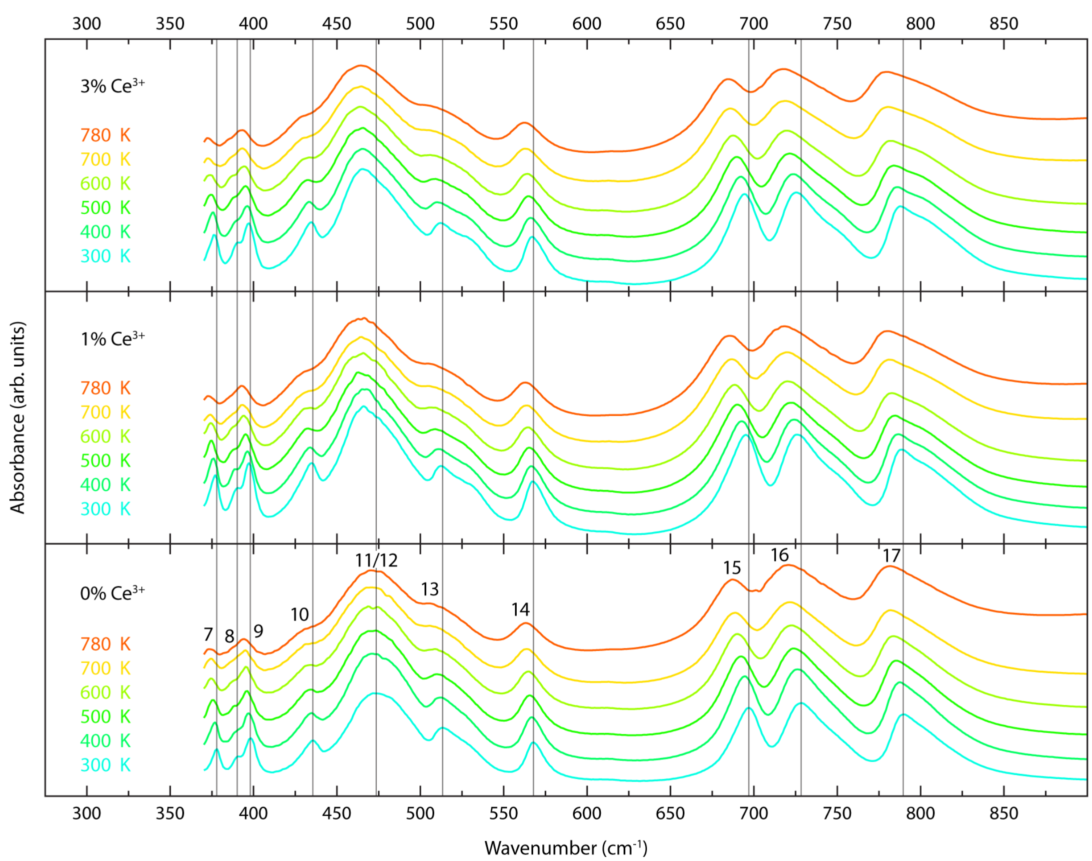

Figure S4 IR spectra of YAG:z%Ce^{3+} ($z = 0$, 1, and 3) in the temperature range of 300–780 K. Vertical lines are positioned at the maxima of the IR bands of YAG at 300 K.

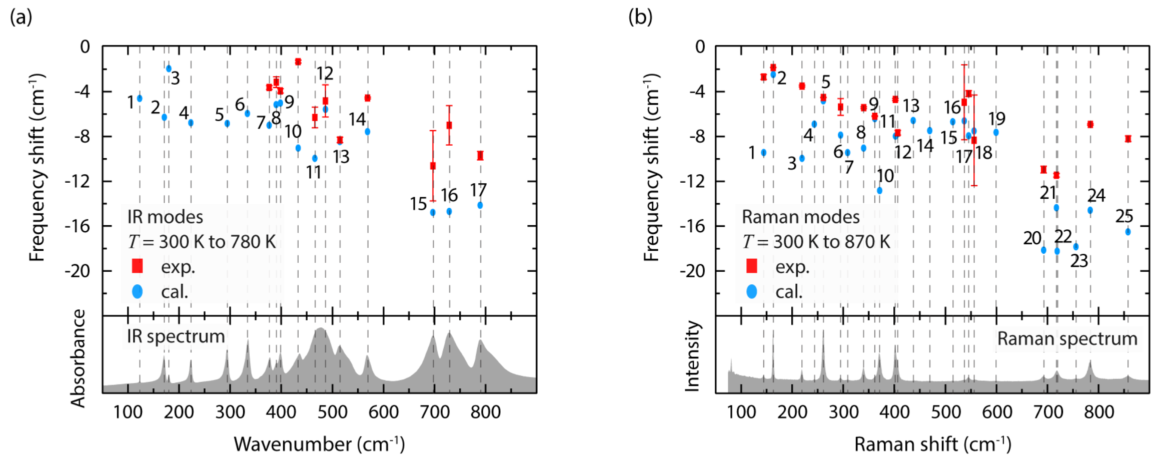

Figure S5 Experimental and calculated vibrational frequency shift of YAG upon increasing temperature (a) from 300 to 780 K for the IR-active modes and (b) from 300 to 870 K for the Raman-active modes.

Table S1 Mathematical description of the symmetry coordinates, $|\eta\rangle$, of cubic YO_8, octahedral AlO_6, and tetrahedral AlO_4 moieties, expressed in terms of the internal coordinates r (bonding length) and θ (bonding angle), cf. Figure S1. Degeneracy of symmetry coordinates is distinguished by the superscripts $'$, $''$ and $'''$.

Displacement	**Symmetry coordinate**
Cubic YO_8	
Symmetric stretching	$A_{1g}^{r} = \frac{1}{2\sqrt{2}}\Delta(r_1 + r_2 + r_3 + r_4 + r_5 + r_6 + r_7 + r_8)$
Asymmetric stretching	$A_{2u}^{r} = \frac{1}{2\sqrt{2}}\Delta(r_1 - r_2 + r_3 - r_4 - r_5 + r_6 - r_7 + r_8)$
Asymmetric stretching	$T_{1u}^{'\,r} = \frac{1}{2\sqrt{6}}\Delta(3r_1 + r_2 - r_3 + r_4 + r_5 - r_6 - 3r_7 - r_8)$
Asymmetric stretching	$T_{1u}^{''\,r} = \frac{1}{2}\Delta(r_2 + r_3 - r_5 - r_8)$
Asymmetric stretching	$T_{1u}^{'''\,r} = \frac{1}{2\sqrt{3}}\Delta(r_2 - r_3 - 2r_4 + r_5 + 2r_6 - r_8)$
Stretching	$T_{2g}^{'\,r} = \frac{1}{2\sqrt{6}}\Delta(3r_1 - r_2 - r_3 - r_4 - r_5 - r_6 + 3r_7 - r_8)$
Stretching	$T_{2g}^{''\,r} = \frac{1}{2}\Delta(r_2 - r_3 - r_5 + r_8)$
Stretching	$T_{2g}^{'''\,r} = \frac{1}{2\sqrt{3}}\Delta(-r_2 - r_3 + 2r_4 - r_5 + 2r_6 - r_8)$
Symmetric bending	$E_{g}^{'\,\theta} = \frac{1}{2\sqrt{6}}\Delta(2\theta_{12} - \theta_{14} - \theta_{15} - \theta_{23} - \theta_{26} + 2\theta_{34} - \theta_{37} - \theta_{48} + 2\theta_{56} - \theta_{58} - \theta_{67} + 2\theta_{78})$
Symmetric bending	$E_{g}^{''\,\theta} = \frac{1}{2\sqrt{6}}\Delta(2\theta_{13} - \theta_{16} - \theta_{18} + 2\theta_{24} - \theta_{25} - \theta_{27} - \theta_{36} - \theta_{38} - \theta_{45} - \theta_{47} + 2\theta_{57} + 2\theta_{68})$
Symmetric twisting	$E_{u}^{'\,\theta} = \frac{1}{2\sqrt{6}}\Delta(2\theta_{13} - \theta_{16} - \theta_{18} - 2\theta_{24} + \theta_{25} + \theta_{27} - \theta_{36} - \theta_{38} + \theta_{45} + \theta_{47} - 2\theta_{57} + 2\theta_{68})$
Symmetric twisting	$E_{u}^{''\,\theta} = \frac{1}{2\sqrt{2}}\Delta(\theta_{16} - \theta_{18} - \theta_{25} + \theta_{27} - \theta_{36} + \theta_{38} + \theta_{45} - \theta_{47})$
Asymmetric bending	$T_{1u}^{'\,\theta} = \frac{1}{4}\Delta(2\theta_{12} + \theta_{14} + \theta_{15} + \theta_{23} + \theta_{26} - \theta_{37} - \theta_{48} - \theta_{58} - \theta_{67} - 2\theta_{78})$
Asymmetric bending	$T_{1u}^{''\,\theta} = \frac{1}{2}\Delta(\theta_{13} + \theta_{24} - \theta_{57} - \theta_{68})$
Asymmetric bending	$T_{1u}^{'''\,\theta} = \frac{1}{4}\Delta(\theta_{14} - \theta_{15} + \theta_{23} - \theta_{26} + 2\theta_{34} + \theta_{37} + \theta_{48} - 2\theta_{56} - \theta_{58} - \theta_{67})$
Bending	$T_{2g}^{'\,\theta} = \frac{1}{2}\Delta(\theta_{12} - \theta_{34} - \theta_{56} + \theta_{78})$
Bending	$T_{2g}^{''\,\theta} = \frac{1}{2}\Delta(\theta_{13} - \theta_{24} + \theta_{57} - \theta_{68})$
Bending	$T_{2g}^{'''\,\theta} = \frac{1}{2}\Delta(\theta_{14} - \theta_{23} - \theta_{58} + \theta_{67})$
Asymmetric twisting	$T_{2u}^{'\,\theta} = \frac{1}{4}\Delta(2\theta_{12} - \theta_{14} - \theta_{15} - \theta_{23} - \theta_{26} + \theta_{37} + \theta_{48} + \theta_{58} + \theta_{67} - 2\theta_{78})$
Asymmetric twisting	$T_{2u}^{''\,\theta} = \frac{1}{4}\Delta(-\theta_{14} + \theta_{15} - \theta_{23} + \theta_{26} + 2\theta_{34} - \theta_{37} - \theta_{48} - 2\theta_{56} + \theta_{58} + \theta_{67})$
Asymmetric twisting	$T_{2u}^{'''\,\theta} = \frac{1}{2\sqrt{2}}\Delta(\theta_{14} - \theta_{15} - \theta_{23} + \theta_{26} + \theta_{37} - \theta_{48} + \theta_{58} - \theta_{67})$

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Table S1 *continued*

Octahedral AlO_6	
Symmetric stretching	$A^{r}_{1g} = \frac{1}{\sqrt{6}}\Delta(r_1 + r_2 + r_3 + r_4 + r_5 + r_6)$
Stretching	$E'^{\,r}_{g} = \frac{1}{2\sqrt{3}}\Delta(2r_1 - r_2 - r_3 - r_4 - r_5 + 2r_6)$
Stretching	$E''^{\,r}_{g} = \frac{1}{2}\Delta(r_2 - r_3 + r_4 - r_5)$
Asymmetric stretching	$T'^{\,r}_{1u} = \frac{1}{\sqrt{2}}\Delta(r_1 - r_6)$
Asymmetric stretching	$T''^{\,r}_{1u} = \frac{1}{\sqrt{2}}\Delta(r_2 - r_4)$
Asymmetric stretching	$T'''^{\,r}_{1u} = \frac{1}{\sqrt{2}}\Delta(r_3 - r_5)$
Asymmetric bending	$T'^{\,\theta}_{1u} = \frac{1}{4}\Delta(2\theta_{12} + \theta_{13} + \theta_{15} + \theta_{23} + \theta_{25} - \theta_{34} - \theta_{36} - \theta_{45} - 2\theta_{46} - \theta_{56})$
Asymmetric bending	$T''^{\,\theta}_{1u} = \frac{1}{2\sqrt{2}}\Delta(\theta_{13} - \theta_{15} + \theta_{23} - \theta_{25} + \theta_{34} + \theta_{36} - \theta_{45} - \theta_{56})$
Asymmetric bending	$T'''^{\,\theta}_{1u} = \frac{1}{4}\Delta(\theta_{13} + 2\theta_{14} + \theta_{15} - \theta_{23} - \theta_{25} - 2\theta_{26} + \theta_{34} - \theta_{36} + \theta_{45} - \theta_{56})$
Bending	$T'^{\,\theta}_{2g} = \frac{1}{2}\Delta(\theta_{12} - \theta_{14} - \theta_{26} + \theta_{46})$
Bending	$T''^{\,\theta}_{2g} = \frac{1}{2}\Delta(\theta_{13} - \theta_{15} - \theta_{36} + \theta_{56})$
Bending	$T'''^{\,\theta}_{2g} = \frac{1}{2}\Delta(\theta_{23} - \theta_{25} - \theta_{34} + \theta_{45})$
Asymmetric bending	$T'^{\,\theta}_{2u} = \frac{1}{4}\Delta(2\theta_{12} - \theta_{13} - \theta_{15} - \theta_{23} - \theta_{25} + \theta_{34} + \theta_{36} + \theta_{45} - 2\theta_{46} + \theta_{56})$
Asymmetric bending	$T''^{\,\theta}_{2u} = \frac{1}{2\sqrt{2}}\Delta(\theta_{13} - \theta_{15} - \theta_{23} + \theta_{25} - \theta_{34} + \theta_{36} + \theta_{45} - \theta_{56})$
Asymmetric bending	$T'''^{\,\theta}_{2u} = \frac{1}{4}\Delta(-\theta_{13} + 2\theta_{14} - \theta_{15} + \theta_{23} + \theta_{25} - 2\theta_{26} - \theta_{34} + \theta_{36} - \theta_{45} + \theta_{56})$
Tetrahedral AlO_4	
Symmetric stretching	$A^{r}_{1} = \frac{1}{2}\Delta(r_1 + r_2 + r_3 + r_4)$
Asymmetric stretching	$T'^{\,r}_{2} = \frac{1}{2\sqrt{3}}\Delta(3r_1 - r_2 - r_3 - r_4)$
Asymmetric stretching	$T''^{\,r}_{2} = \frac{1}{\sqrt{2}}\Delta(r_2 - r_3)$
Asymmetric stretching	$T'''^{\,r}_{2} = \frac{1}{\sqrt{6}}\Delta(r_2 + r_3 - 2r_4)$
Symmetric bending	$E'^{\,\theta} = \frac{1}{2\sqrt{3}}\Delta(2\theta_{12} - \theta_{13} - \theta_{14} - \theta_{23} - \theta_{24} + 2\theta_{34})$
Symmetric bending	$E''^{\,\theta} = \frac{1}{2}\Delta(\theta_{13} - \theta_{14} - \theta_{23} + \theta_{24})$
Asymmetric bending	$T'^{\,\theta}_{2} = \frac{1}{\sqrt{2}}\Delta(\theta_{12} - \theta_{34})$
Asymmetric bending	$T''^{\,\theta}_{2} = \frac{1}{\sqrt{2}}\Delta(\theta_{13} - \theta_{24})$
Asymmetric bending	$T'''^{\,\theta}_{2} = \frac{1}{\sqrt{2}}\Delta(\theta_{14} - \theta_{23})$

Table S2 Compilation of the Debye temperature θ_D (in units of Kelvin), of YAG with lattice constant a at the environmental temperatures of 300, 500 and 1200 K that is denoted by $a_{300\text{ K}}$, $a_{500\text{ K}}$, and $a_{1200\text{ K}}$, respectively, where $a_{1200\text{ K}} > a_{500\text{ K}} > a_{300\text{ K}}$. θ_D is derived from the mean-square-displacement $\langle u^2 \rangle$ through $\langle u^2 \rangle = \frac{3\hbar^2}{mk_BT}(\frac{1}{x^2})(1+\frac{x^2}{36}-\frac{x^4}{3600})$, where $x = \theta_D/T$ and m is the mass of the atom, see ref S1 for details.

YAG	$a_{300\text{ K}}$		$a_{500\text{ K}}$		$a_{1200\text{ K}}$	
Atoms	$\langle u^2 \rangle$ (Å^2)	θ_D (K)	$\langle u^2 \rangle$ (Å^2)	θ_D (K)	$\langle u^2 \rangle$ (Å^2)	θ_D (K)
Y	0.003891	362.28	0.006940	345.67	0.018951	322.27
Al^{VI}	0.003638	715.07	0.005930	691.74	0.014748	665.27
Al^{IV}	0.003406	742.58	0.005401	726.64	0.012932	710.88
O	0.004670	837.99	0.007407	811.02	0.017979	783.75
Average		740.03		716.63		691.75

References

(S1) Willis, B. T. M.; Pryor, A. W. *Thermal Vibrations in Crystallography*; Cambridge University Press, 1975.