Structural and mechanical properties of Y_2SiO_5-Lu_2SiO_5 solid solutions from *ab initio* calculations

Supplementary Information S2:
Transformation from primitive to conventional unit cell (in B2/b setting)

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Step 1. Primitive unit cell parameters

To reduce the computational efforts in the performed calculations, the YSO-LYSO-LSO structures were described using a primitive unit cells containing 32 atoms (the setting preferred by the CRYSTAL code). The lattice parameters include the primitive translation vectors a_p, b_p, c_p, as well as the interaxial angles $\alpha_p = \angle(b_p, c_p)$, $\beta_p = \angle(a_p, c_p)$, and $\gamma_p = \angle(a_p, b_p)$. It should be noted that the choice of primitive lattice vectors is not unique, and multiple equivalent representations of the same lattice can be constructed by different choices of basis vectors. In the present work, the primitive unit cell employed in the calculations corresponds to the default choice implemented in the CRYSTAL code.

As an illustrative example, we consider the primitive unit cell used in the calculations of pure Lu_2SiO_5 (LSO). For all other compositions, equivalent transformations were applied following the same set of formulas described above. For the used LSO primitive cell:

$$a_p = b_p = 7.83584\,\text{Å}, \quad c_p = 10.07871\,\text{Å}, \tag{1}$$

$$\alpha_p = 60.9319^\circ, \quad \beta_p = 119.0681^\circ, \quad \gamma_p = 130.6137^\circ. \tag{2}$$

The relation $\alpha_p + \beta_p = 180^\circ$ indicates that the structure is expressed in a non-conventional primitive setting of a monoclinic lattice. The volume of primitive cell then is equal to $V_p = 396.96\,\text{Å}^3$.

Step 2. Primitive basis vectors in Cartesian coordinates

The primitive basis vectors $\mathbf{v}_1$, $\mathbf{v}_2$, $\mathbf{v}_3$ could be expressed in an orthonormal Cartesian basis [1] by placing $\mathbf{v}_1$ along $\hat{x}$ and $\mathbf{v}_2$ in the $\hat{x}$–$\hat{y}$ plane (here, $\mathbf{v}_1$, $\mathbf{v}_2$, and $\mathbf{v}_3$ represent the primitive lattice vectors corresponding to the lattice parameters a_p, b_p, and c_p, respectively):

$$\mathbf{v}_1 = \begin{pmatrix} a_p \\ 0 \\ 0 \end{pmatrix}, \qquad \mathbf{v}_2 = \begin{pmatrix} b_p \cos\gamma_p \\ b_p \sin\gamma_p \\ 0 \end{pmatrix}. \tag{3}$$

For $\mathbf{v}_3$ we define explicitly:

$$v_{3x} = c_p \cos\beta_p, \quad v_{3y} = \frac{c_p(\cos\alpha_p - \cos\beta_p \cos\gamma_p)}{\sin\gamma_p}. \tag{4}$$

The third component can be written either geometrically or via the cell volume:

$$v_{3z} = \sqrt{c_p^2 - v_{3x}^2 - v_{3y}^2} = \frac{V_p}{a_p b_p \sin\gamma_p}. \tag{5}$$

This transformation from the unit cell basis to an orthonormal basis could ber applied to any crystal structure, while higher-symmetry systems represent special cases of this formulation.

Substituting the numerical values:

$$\begin{aligned} \cos\gamma_p &= -0.650956, & \sin\gamma_p &= 0.759115, \\ \cos\beta_p &= -0.485849, & \cos\alpha_p &= 0.485849, \end{aligned}$$

Here, $\cos\gamma_p$ and $\sin\gamma_p$ correspond to the cosine and sine of the angle γ_p between the primitive lattice vectors a_p and b_p, while $\cos\beta_p$ and $\cos\alpha_p$ denote the cosines of the angles β_p and α_p between the vector pairs (a_p, c_p) and (b_p, c_p), respectively.

$$\begin{aligned} v_{1x} &= 7.83584\,\text{Å}, \\ v_{2x} &= -5.10079\,\text{Å}, \quad v_{2y} = 5.94830\,\text{Å}, \\ v_{3x} &= -4.89674\,\text{Å}, \quad v_{3y} = 2.25154\,\text{Å}, \quad v_{3z} = 8.51663\,\text{Å}, \end{aligned} \tag{6}$$

where v_{1x} is the Cartesian component of the primitive lattice vector $\mathbf{v}_1$ along the $\hat{x}$ direction (with $v_{1y} = v_{1z} = 0$ by construction). The quantities v_{2x} and v_{2y} are the Cartesian components of the vector $\mathbf{v}_2$ in the $\hat{x}$ and $\hat{y}$ directions, respectively (with $v_{2z} = 0$), while v_{3x}, v_{3y}, and v_{3z} denote the Cartesian components of the vector $\mathbf{v}_3$ along the $\hat{x}$, $\hat{y}$, and $\hat{z}$ axes, respectively. Thus,

$$\mathbf{v}_1 = \begin{pmatrix} 7.83584 \\ 0 \\ 0 \end{pmatrix} \text{Å}, \quad \mathbf{v}_2 = \begin{pmatrix} -5.10079 \\ 5.94830 \\ 0 \end{pmatrix} \text{Å}, \quad \mathbf{v}_3 = \begin{pmatrix} -4.89674 \\ 2.25154 \\ 8.51663 \end{pmatrix} \text{Å}. \tag{7}$$

Step 3. Transformation matrix from primitive to conventional unit cell

The conventional B 2/b cell vectors $\{\mathbf{B}_a, \mathbf{B}_b, \mathbf{B}_c\}$ are expressed as integer linear combinations of the primitive vectors:

$$\begin{pmatrix} \mathbf{B}_a \\ \mathbf{B}_b \\ \mathbf{B}_c \end{pmatrix} = \underbrace{\begin{pmatrix} 1 & -1 & 0 \\ -1 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}}_{\mathbf{M}} \begin{pmatrix} \mathbf{v}_1 \\ \mathbf{v}_2 \\ \mathbf{v}_3 \end{pmatrix}. \tag{8}$$

The determinant $\det\mathbf{M} = -2$, hence the conventional unit cell volume V_{conv} is two times larger than the primitive unit cell volume V_{p}:

$$V_{\text{conv}} = |\det\mathbf{M}|\, V_p = 2V_p = 793.92\,\text{Å}^3. \tag{9}$$

Note that for space group Nr. 15 the transformation matrix is not unique; it produces an equivalent monoclinic conventional cell that may differ from the used B2/b setting by axis permutation, rotation, or transformation to I2/a setting.

Using the transformation matrix $\mathbf{M}$, the conventional lattice vectors are obtained as linear combinations of the primitive vectors:

$$\mathbf{B}_a = \mathbf{v}_1 - \mathbf{v}_2, \quad \mathbf{B}_b = -\mathbf{v}_1 - \mathbf{v}_2, \quad \mathbf{B}_c = \mathbf{v}_3. \tag{10}$$

Substituting the Cartesian components of the primitive vectors yields:

$$\mathbf{B}_a = \begin{pmatrix} 7.83584 - (-5.10079) \\ 0 - 5.94830 \\ 0 \end{pmatrix} = \begin{pmatrix} 12.93663 \\ -5.94830 \\ 0 \end{pmatrix} \text{ Å}, \tag{11}$$

$$\mathbf{B}_b = \begin{pmatrix} -7.83584 - (-5.10079) \\ 0 - 5.94830 \\ 0 \end{pmatrix} = \begin{pmatrix} -2.73505 \\ -5.94830 \\ 0 \end{pmatrix} \text{ Å}, \tag{12}$$

$$\mathbf{B}_c = \begin{pmatrix} -4.89674 \\ 2.25154 \\ 8.51663 \end{pmatrix} \text{ Å}. \tag{13}$$

Step 4. Lattice parameters of the conventional unit cell

Lengths: The lengths of the conventional lattice vectors are obtained as

$$a = |\mathbf{B}_a| = \sqrt{12.93663^2 + (-5.94830)^2} = 14.239\,\text{Å}, \tag{14}$$

$$b = |\mathbf{B}_b| = \sqrt{(-2.73505)^2 + (-5.94830)^2} = 6.547\,\text{Å}, \tag{15}$$

$$c = |\mathbf{B}_c| = \sqrt{(-4.89674)^2 + 2.25154^2 + 8.51663^2} = 10.079\,\text{Å}. \tag{16}$$

Angles: The interaxial angles are obtained from scalar products of the vectors.

$$\begin{aligned} \mathbf{B}_a \cdot \mathbf{B}_b &= (12.93663)(-2.73505) + (-5.94830)(-5.94830) + 0 \\ &= -35.382 + 35.382 = 0, \\ \cos\gamma &= \frac{\mathbf{B}_a \cdot \mathbf{B}_b}{|\mathbf{B}_a||\mathbf{B}_b|} = 0, \quad \gamma = 90^\circ. \end{aligned} \tag{17}$$

$$\begin{aligned} \mathbf{B}_b \cdot \mathbf{B}_c &= (-2.73505)(-4.89674) + (-5.94830)(2.25154) + 0 \cdot 8.51663 \\ &= 13.393 - 13.393 = 0, \\ \cos\alpha &= \frac{\mathbf{B}_b \cdot \mathbf{B}_c}{|\mathbf{B}_b||\mathbf{B}_c|} = 0, \quad \alpha = 90^\circ. \end{aligned} \tag{18}$$

$$
\begin{aligned}
\mathbf{B}_a \cdot \mathbf{B}_c &= (12.93663)(-4.89674) + (-5.94830)(2.25154) + 0 \cdot 8.51663 \\
&= -63.347 - 13.393 = -76.756, \\
\cos\beta &= \frac{\mathbf{B}_a \cdot \mathbf{B}_c}{|\mathbf{B}_a||\mathbf{B}_c|} = \frac{-76.756}{14.239 \times 10.079} = \frac{-76.756}{143.513} = -0.5349, \\
\beta &= \arccos(-0.5349) = 122.33^\circ.
\end{aligned} \tag{19}
$$

Summary

Thus, for pure LSO, the 32-atom primitive unit cell employed in the CRYSTAL calculations was transformed into the equivalent 64-atom conventional unit cell in the B2/b setting. The unit-cell volume increases from $V_p = 396.96\,\text{Å}^3$ to $V_{\text{conv}} = 793.92\,\text{Å}^3$, i.e. exactly by a factor of two, in agreement with the determinant of the transformation matrix, $\det\mathbf{M} = -2$. The transformation to the I2/a setting, which represents an alternative crystallographic description of the system, can be performed starting from the B2/b cell obtained here using the transformation matrix $\mathbf{T}_{\text{B2/b}\rightarrow\text{I2/a}}$ provided in the main text of the article.

Table 1: Transformation of the 32-atom primitive LSO unit cell used in the CRYSTAL calculations to the equivalent 64-atom conventional unit cell in the B2/b setting. In the literature, two equivalent monoclinic descriptions are commonly used, namely the B-centered (B2/b) and the body-centered (I2/a) settings. The increase of the cell volume from V_p to $V_{\text{conv}} = 2V_p$ is consistent with the transformation matrix determinant $|\det\mathbf{M}| = 2$.

Parameter	Primitive (32 atoms)	Conventional $B\,2/b$ (64 atoms)
a (Å)	7.836	14.239
b (Å)	7.836	6.547
c (Å)	10.079	10.079
α (°)	60.93	90.00
β (°)	119.07	122.33
γ (°)	130.61	90.00
V (Å^3)	396.96	793.92

References

[1] D. W. Bennett, *Understanding Single-Crystal X-Ray Crystallography*, Wiley-VCH Verlag GmbH & Co. KGaA, 2010.