SUPPORTING INFORMATION

Ambient-Pressure Synthesis of SHG-Active $\text{Eu}_2\text{Ti}_2\text{O}_7$ with a [110] Layered Perovskite Structure: Suppressing Pyrochlore Formation by Oxidation of Perovskite-Type EuTiO_3

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Ferroelectricity Measurement

$\text{La}_2\text{Ti}_2\text{O}_7$ is ferroelectric at room temperature. The Eu-containing structural analog, however, does not exhibit ferroelectric properties, as shown in Figure S1.

Figure S1. Ferroelectric response of perovskite-type $\text{Eu}_2\text{Ti}_2\text{O}_7$. No hysteresis is observed.

Structure of $\text{Eu}_2\text{Ti}_2\text{O}_7$

The broad diffraction peaks in the XRD data for $\text{Eu}_2\text{Ti}_2\text{O}_7$ formed by the oxidation of EuTiO_3 make structure refinement difficult, precluding definitive determination of whether perovskite-type $\text{Eu}_2\text{Ti}_2\text{O}_7$ crystallizes in a monoclinic or orthorhombic space group (in analogy to the two modifications of $\text{La}_2\text{Ti}_2\text{O}_7$). As shown in Figure S2, both modifications (monoclinic and orthorhombic) yield very similar diffraction patterns. Reflections that would distinguish between the $P2_1$ and $Pna2_1$ space groups have a low relative intensity and are difficult to detect. A small shoulder at low angles (14.2° 2-theta), as well as a few low-intensity peaks (e.g. 35.6 and 36.2° 2-theta), are consistent with the monoclinic form of $\text{Eu}_2\text{Ti}_2\text{O}_7$, although this assignment is not absolute and cannot be definitively determined based on the available data. This proposed assignment (monoclinic $\text{Eu}_2\text{Ti}_2\text{O}_7$) is also consistent with the room-temperature monoclinic structure of $\text{La}_2\text{Ti}_2\text{O}_7$.

Figure S2. Comparison of simulated XRD patterns for the possible orthorhombic and monoclinic modifications of perovskite-type $\text{Eu}_2\text{Ti}_2\text{O}_7$ (modeled based on the corresponding structures of $\text{La}_2\text{Ti}_2\text{O}_7$ and lattice constants determined from the $\text{Eu}_2\text{Ti}_2\text{O}_7$ data). Diffraction peaks and shoulders that suggest the monoclinic structure are indicated in the highlighted areas. The fact that the room-temperature structure of $\text{La}_2\text{Ti}_2\text{O}_7$ is monoclinic provides further support for the hypothesis that $\text{Eu}_2\text{Ti}_2\text{O}_7$ exists in the monoclinic form at room temperature.

Structure Refinement

To supplement the visual comparison between simulated and experimental data presented in Figure 2 of the main text, a Rietveld analysis has been performed. Below is a more detailed background-subtracted comparison showing the overlay between the observed and simulated data. The fit is not ideal because of the reasons discussed in the text (limited crystallinity, likely a consequence of the low-temperature preparation method, makes the profile difficult to fit). Thus, while we cannot draw too many conclusions from the refinement, it reinforces the structural similarities between $\text{La}_2\text{Ti}_2\text{O}_7$ and $\text{Eu}_2\text{Ti}_2\text{O}_7$.

Figure S3. Rietveld refinement for layered-perovskite type $\text{Eu}_2\text{Ti}_2\text{O}_7$. The difference curve (bottom, solid) indicates the level of agreement between the calculated (red) and observed patterns. $R_{\text{exp}} = 5.98$, $R_{\text{wp}} = 12.69$, $R_p = 10.07$, and $\text{GOF} = 2.12$.

Atom labels for $\text{Eu}_2\text{Ti}_2\text{O}_7$

In the text, the titanium atoms are discussed as Ti(1), Ti(2), Ti(3), and Ti(4). The locations of these titanium atoms are shown below.

Figure S4. Crystal structure of layered perovskite $\text{Eu}_2\text{Ti}_2\text{O}_7$. Each of the Ti^{4+} cations are shifted away from the center of the TiO_6 octahedra. The dashed black line represents the monoclinic unit cell.