

## Supplementary Information

### Precursor Analysis and Reaction Mechanism

The formation of the precursors can be divided into two reactions:

In **a)**, metallic Ba reacts with the alcohol used to form the barium alkoxide, releasing hydrogen gas (see Fig. S.1).

In **b)**, as proposed by M. Niederberger et al., the employed alcohol (OLOH or BzOH) coordinates to a Ti atom, proposed as a five-fold coordination complex.<sup>41</sup> This coordination weakens the C-O bond of the alcohol, which activates its  $\alpha$ -carbon for a nucleophilic attack. Then, one of the two  $\beta$ -carbon atoms of the isopropoxy group is deprotonated (**1**). The alcoholate, produced in the reaction in Fig. S.1 **a)**, likely acts as the base in this deprotonation. This process is supported by a stabilizing C-Ti interaction (**2**), which explains why the deprotonation occurs at the  $\beta$ -site rather than the  $\alpha$ -carbon of the isopropoxy group. This leads to a hexacoordinated Ti center.<sup>41</sup> The close proximity of the methyl group and the formal carbanion within the titanium octahedron intermediate facilitates a rapid nucleophilic attack, resulting in a titanium complex with the coordinated OLOH or BzOH residue and a coordinated OH-group (**3**). The OH-group facilitates the condensation of the titanium monomer into a Ti-O-Ti species via alcohol elimination.<sup>41</sup>

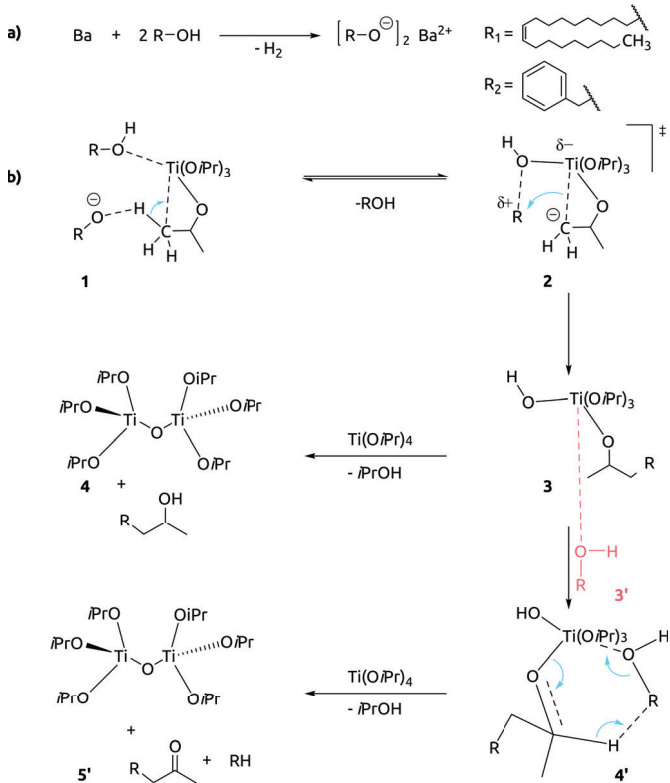


Fig. S.1 Reaction mechanism for the white precursor precipitate proposed by M. Niederberger et al.<sup>41</sup> It consists of the a) barium alkoxide and b) Ti-O-Ti species, with a side reaction, similar to the Meerwein-Ponndorf-Verley reduction. The side reaction path is marked with an apostrophe. Figure b) adapted from M. Niederberger et al.<sup>41</sup>

In a potential side reaction (steps **3**, **4'** and **5'**) another benzyl

alcohol molecule coordinates to the Ti of the complex in step **3**, creating a very electrophilic benzylic carbon atom.<sup>41</sup> In the next step, a hydride is transferred from the  $\alpha$ -carbon, similar to the Meerwein-Ponndorf-Verley reduction. Here, the employed alcohol is reduced by the oxidation of the formed alcohol (in step **4**), which then results in the same Ti-O-Ti species, an alkene, and a ketone as side products (**5'**) (see Fig. S.1 **b)**).

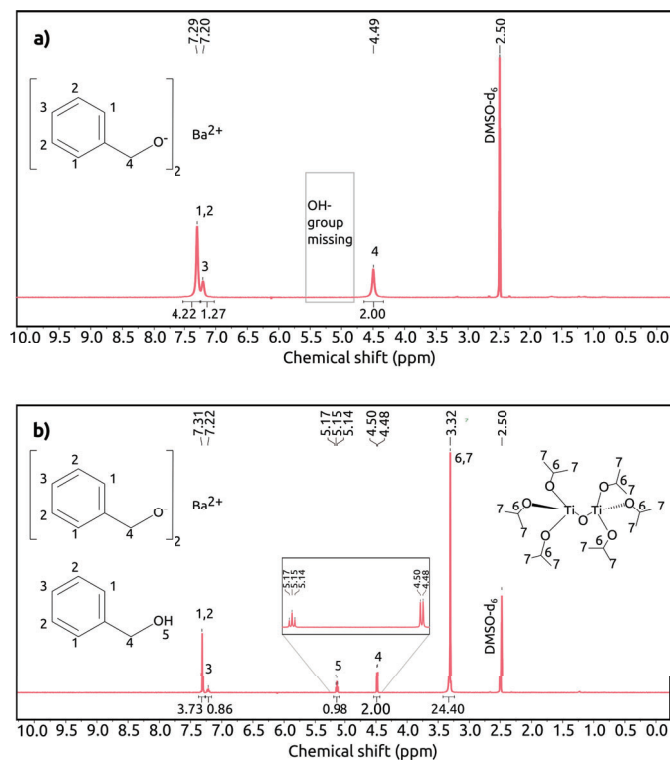


Fig. S.2 <sup>1</sup>H NMR spectra (400 MHz, DMSO-d<sub>6</sub>, 278 K) of a) the vacuum dried barium alkoxide and b) the vacuum dried white precipitate containing the barium alkoxide as well as the Ti complex (suggested in Fig. S.1 b) in step 4 and 5'.

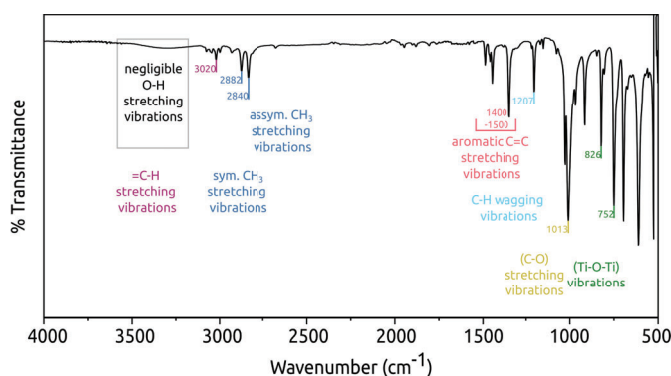


Fig. S.3 FT-IR spectra of the vacuum dried white precipitate containing the barium alkoxide as well as the Ti complex suggested in Fig. S.1 b) in step 4 and 5'.

The slight decrease between 3000  $\text{cm}^{-1}$  -3500  $\text{cm}^{-1}$  observed in the spectrum in Figure S.3 can be attributed to atmospheric mois-

ture, as the measurement was conducted in air. Due to the substantial change in dipole moment during the OH stretch, the OH peak in FT-IR spectroscopy is a high intensity peak.<sup>58</sup> Therefore, this minor signal does not originate from an OH-group in the precursor and can be neglected.

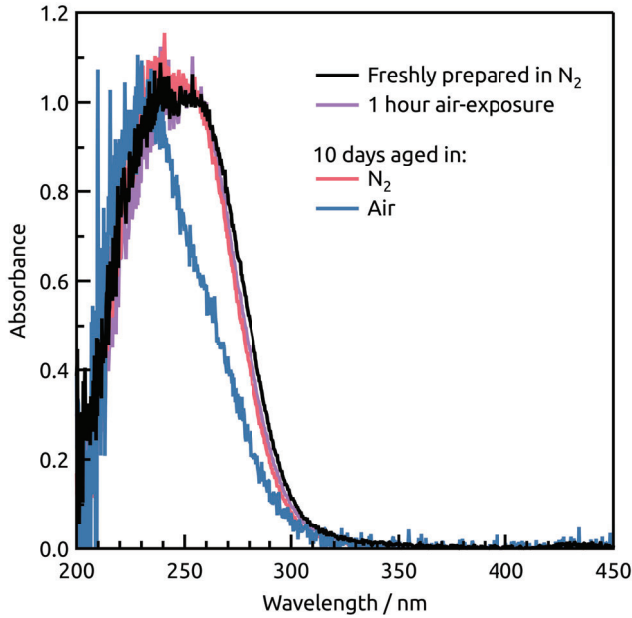


Fig. S.4 Absorbance spectra of the barium-titanium oleyl alkoxide precursor as prepared in the glove box and after the listed aging and stability tests. When stored in nitrogen, the precursor has negligible changes over time. Limited air-exposure (ca. 1 hour) shows minimal degradation.

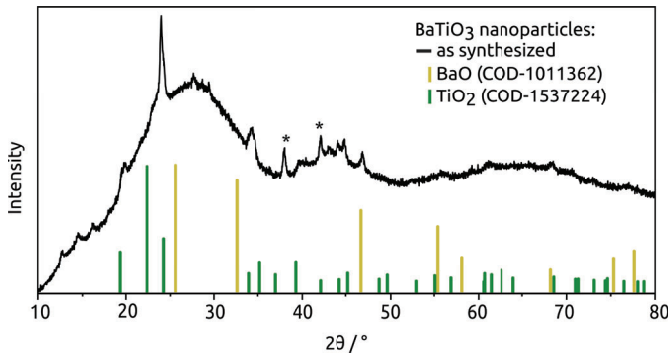


Fig. S.5 Exemplary XRD patterns of the synthesized binary oxide particles. The reflection at 38° and 42° in the XRD data can be attributed to interference caused by the substrate holder with the measurement signal and is marked with a \*. The BaO and TiO<sub>2</sub> reference patterns are retrieved from the Crystallography Open Database (COD), accessed in June 2024.

### Ligand Exchange with KOH

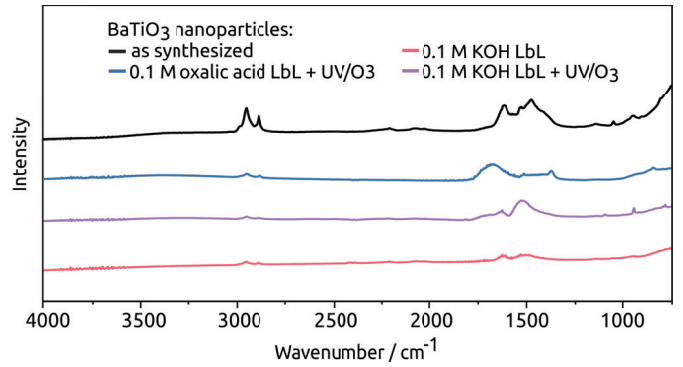


Fig. S.6 FT-IR spectra of the BaTiO<sub>3</sub> with and without the LbL ligand exchange and with and without UV/O<sub>3</sub> cleaning the sample for 30 min. The samples were measured on ITO. Note an offset for clarity.

### Structures of the Slabs

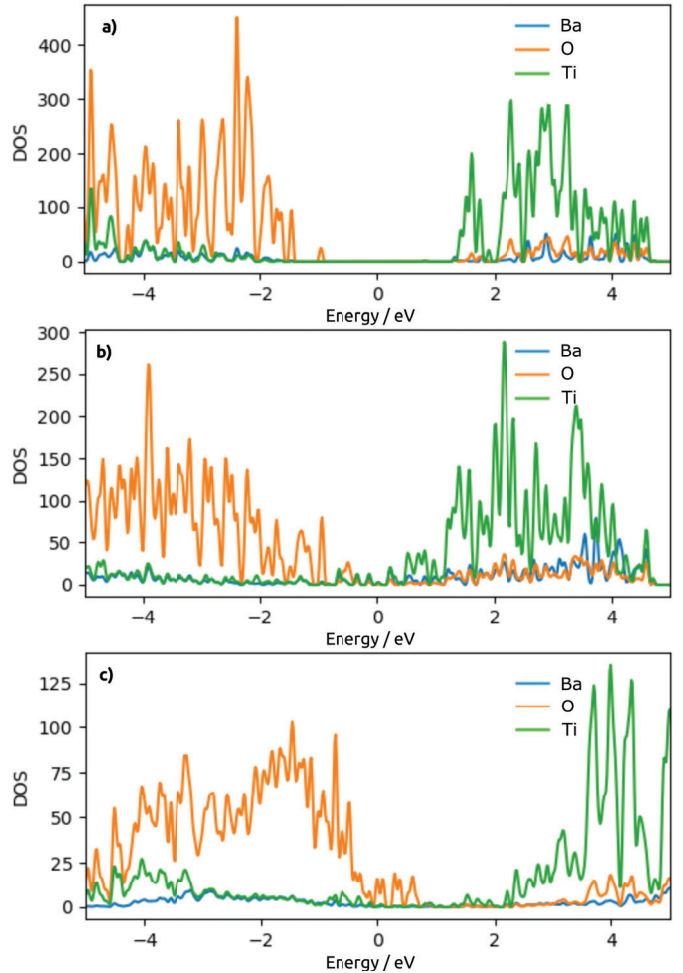


Fig. S.7 Projected DOS plots for the slabs with a) 100, b) 110, and c) 111 surfaces exposed.

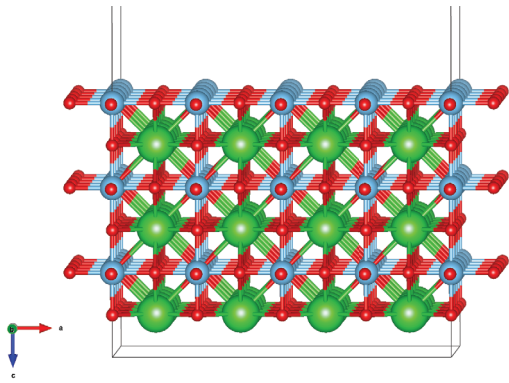


Fig. S.8 (100)-terminated slab. The blue, green, and red spheres represent Ti, Ba, and O atoms, respectively.

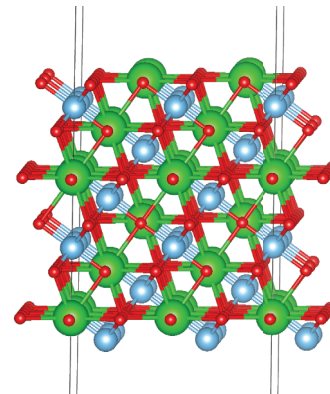


Fig. S.10 (111)-terminated slab. The blue, green, and red spheres represent Ti, Ba, and O atoms, respectively.

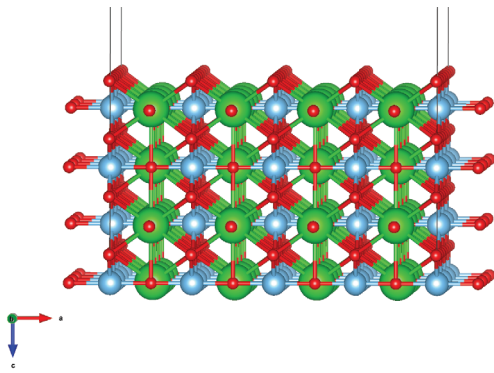
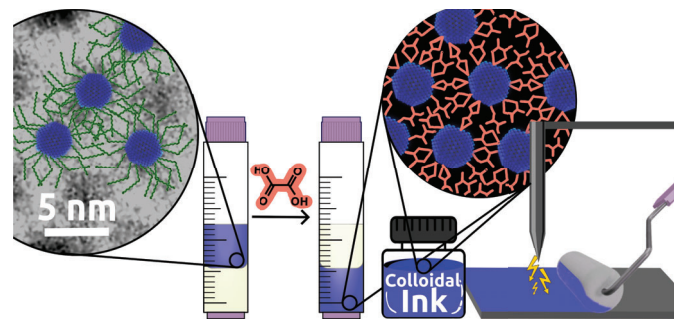


Fig. S.9 (110)-terminated slab. The blue, green, and red spheres represent Ti, Ba, and O atoms, respectively.

### TOC



Colloidal  $\text{BaTiO}_3$  nanoparticles were synthesized, ligand exchanged with oxalic acid to make an ink, and their properties explored for piezoelectric applications.