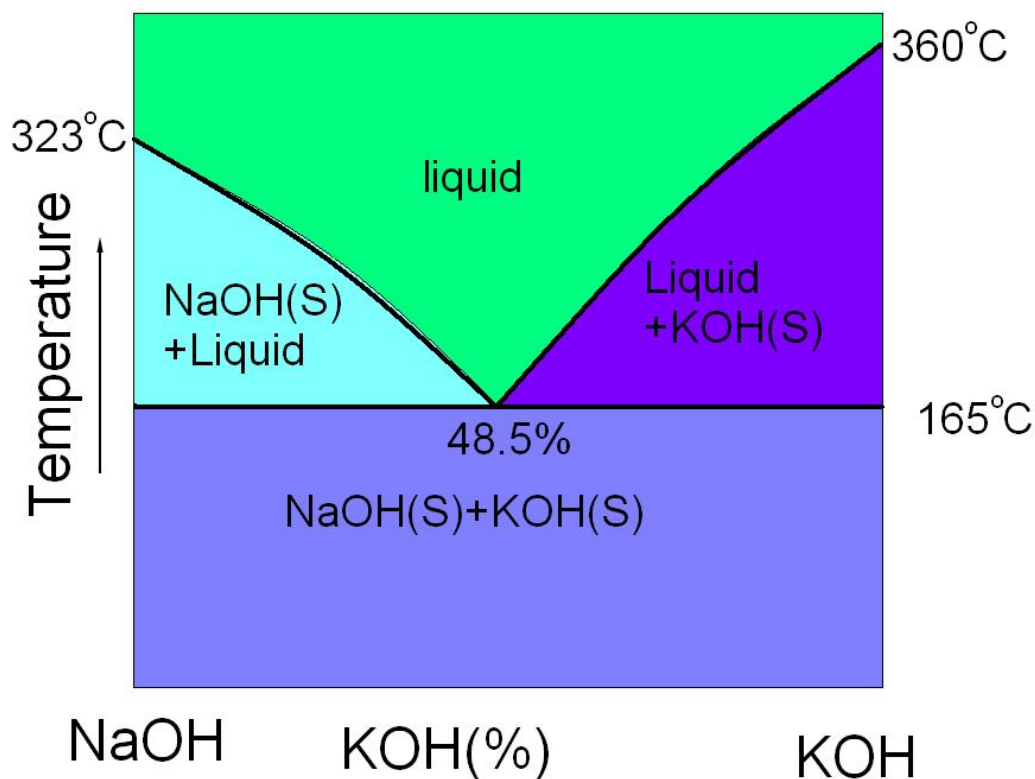


Supplementary Materials

Composite-hydroxide-mediated approach for the synthesis of nanostructures of complex functional-oxides

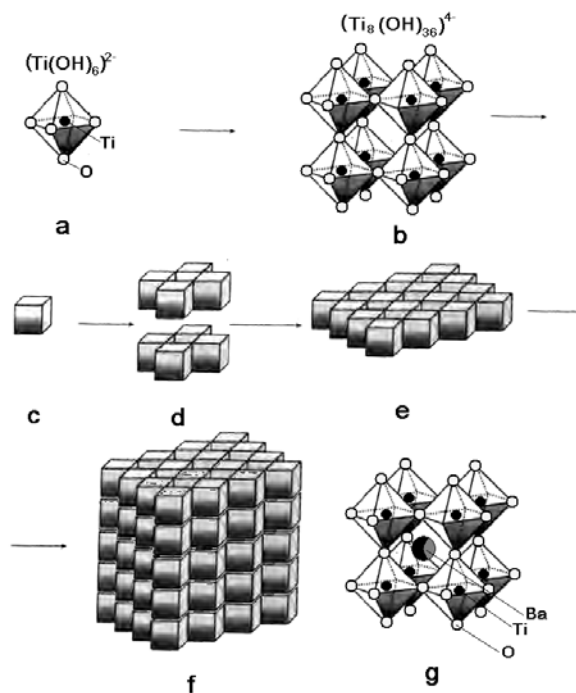
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Schematic phase diagram of NaOH-KOH. Melting points of potassium hydroxide and sodium hydroxide are 323 and 360°C, respectively. The eutectic point at NaOH/KOH=51.5:48.5 is only about 165°C. This is the key for lowering the reaction temperature in our proposed approach.

Fig S7.

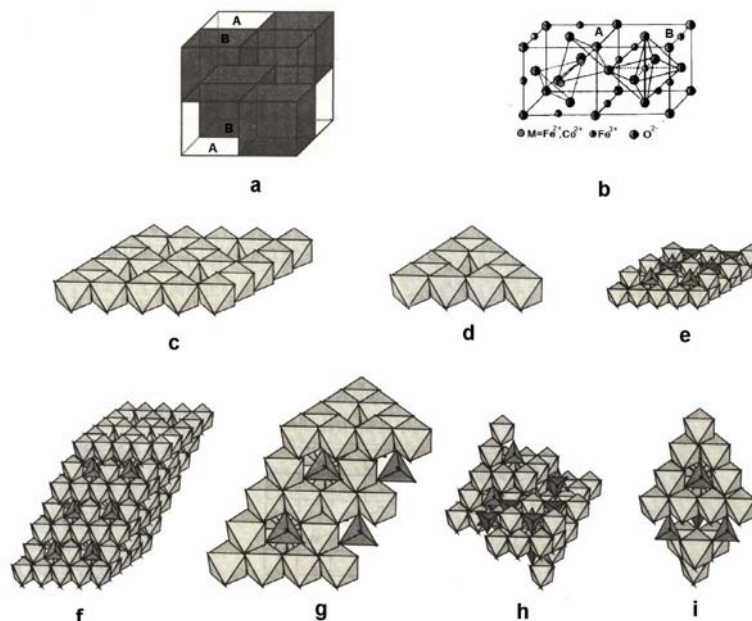
Formation process of provskite BaTiO₃ nanocubes.



When the mixed hydroxides melt at higher temperature, the liquid consists of only two kinds cations, Na⁺ and K⁺, and anions, OH⁻. The solvent is a kind of ionic liquid at this temperature. For the B site oxides, such as TiO₂ they dissolve in the ionic liquid, and form Ti⁴⁺ ions. Because there are a lot of OH⁻ adjacent to the cation, Ti⁴⁺ in the solution, Ti⁴⁺ can link with hydroxyl ions and form a (Ti(OH)₆)²⁻ octahedron. The octahedral link together by polycondensation reaction among them and form one, two or three dimensional structures under different conditions.

Now we look at the formation of provskite. Figure S7 shows (Ti(OH)₆)²⁻ octahedron and polycondensation reaction and the stacking of the growth units. Fig S7a shows a (Ti(OH)₆)²⁻ group. Eight groups link together through 12 bridged oxygen atoms and form a (Ti₈(OH)₃₆)⁴⁻ group (Fig. S7b). (Ti₈(OH)₃₆)⁴⁻ groups link together and form a 2-dimensional structure (Fig. S7c, d, and e). The planar unit cell stack together and forms a 3-dimensional frame (Fig. S7f). This kind of frame can be the template for forming cubic BaTiO₃ nanostructure when TiO₂ reacts with Ba²⁺ in molten hydroxide ionic liquid (Fig S7g). During the formation of BaTiO₃ nanocubes, the framework made by (Ti(OH)₆)²⁻ functions as a capping agent [Hertl, W. Kinetics of barium titanate synthesis. *J. Am. Ceram. Soc.*, **71**, 879-883 (1988); Kutty, T. W. N., Vivekanandan, R., and Murugaraj, P. Precipitation of rutile and anatase (TiO₂) fine powders and their conversion to MTiO₃(M=ba, Sr, Ca) by the hydrothermal method. *Mater. Chem. Phys.*, **19**, 533-546 (1988)].

Fig S8
Spinal MF_2O_4 crystalline cell and possible growth units.



When the mixed hydroxides melt at higher temperature, the liquid consists of only two kinds cations, Na^+ and K^+ , and anions, OH^- . The solvent is a kind of ionic liquid at this temperature. For the B site oxides, such as Fe_2O_3 they dissolve in the ionic liquid, and form Fe^{3+} ions. Because there are a lot of OH^- adjacent to the action, Fe^{3+} in the solution, Fe^{3+} can link with hydroxyl ions and form a $(\text{Fe}(\text{OH})_6)^{3-}$ octahedron. The octahedra link together by polycondensation reaction among them and form one, two or three dimensional structures under different conditions.

Figure S8 shows some growth unit models of spinal crystals. Figures S8a and b are the crystalline unit of MFe_2O_4 spinels. Fe^{3+} can also link with OH^- s and form $(\text{Fe}(\text{OH})_6)^{3-}$ groups in molten hydroxide solvent, and form different packing configurations. These different structure frame built by $(\text{Fe}(\text{OH})_6)^{3-}$ groups will be the template for forming MFe_2O_4 spinal crystals. These packing blocks of $(\text{Fe}(\text{OH})_6)^{3-}$ link with $(\text{M}(\text{OH})_4)^{2-}$ tetrahedrons and form 7 kinds of MFe_2O_4 spinal growth units (Fig. S8c-i). The result of calculation of steady energy on all these possible growth units shows that the most possible growth unit should be Fig. S8i, and the morphology of spinal crystal is a regular octahedron [E. W. Shi, et al. An introduction to computational crystallography: The relationship between aluminum based spinal structures and their morphologies, *Sic. In China* **46**, 259-270 (2003); E. W. Shi, et al. An introduction to computational crystallography: The relationship between aluminum based spinal structures and their morphologies, *Sic. In China* **46**, 259-270 (2003)]. Other growth units in Figure S8 are unlikely. However, in our study, we have found FeFe_2O_4 nanocubes and nanocuboids, and even found CoFe_2O_4 nanobelts. The morphology of CoFe_2O_4 nanobelts should from one of the planar growth unit, such as c, d, or e, which are impossible in crystal growth in water. The morphology of FeFe_2O_4 nanocubes and nanocuboids should also from another new growth unit. As is well known, in crystal growth, some trace impurity can change the morphology of the crystal. In our study, the large amount of ions will change the crystalline field of the cations and change the packing mode of the polyhedrons. In addition, the high viscosity should be another reason for deviation of the crystal shape from the regular shape of the nanocrystals.