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Supplementary Information

Revealing the hydrothermal crystallization mechanism of ilmenite-type sodium niobate microplates: the roles of potassium ions

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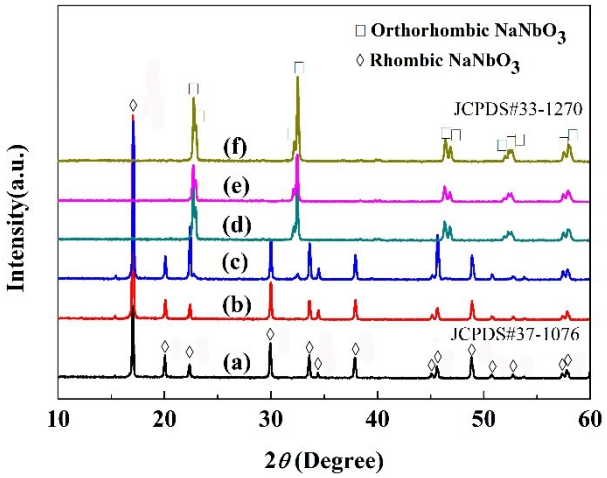

Figure S1. XRD patterns of $NaNbO_3$ prepared at 220 °C for 16 h with KOH (0.5 M) and different content of NaAc: (a) 0.25 M, (b) 0.4 M, (c) 0.5 M, (d) 0.75 M, (e) 1.0 M, (f) 1.5 M.

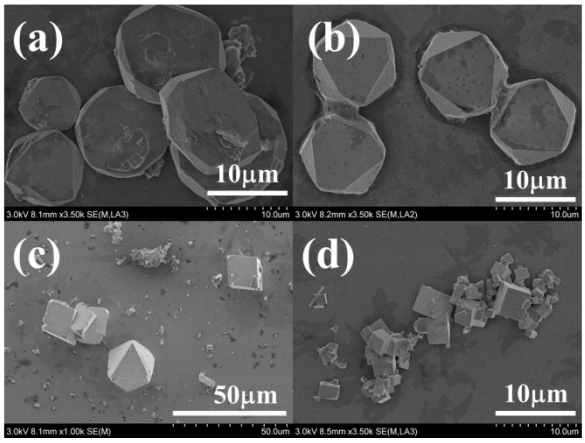

Figure S2. FE-SEM images of $NaNbO_3$ prepared at 220 °C for 16 h with KOH (0.5 M) and different content of NaAc: (a) 0.25 M, (b) 0.4 M, (c) 0.5 M, (d) 1.5 M.

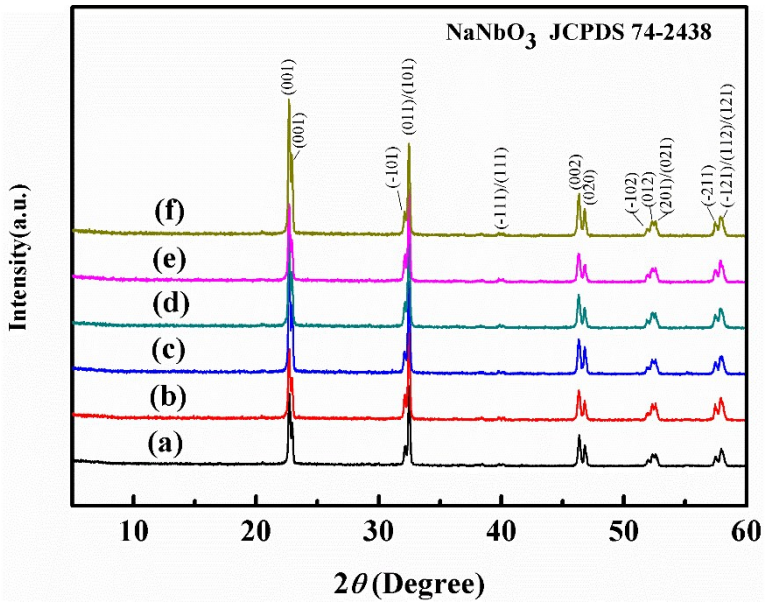

Figure S3. XRD patterns of $NaNbO_3$ prepared at 220 °C for 16 h with NaAc (1.0 M) and different content of KOH: (a) 0.3 M, (b) 0.5 M, (c) 0.8 M, (d) 1.0 M, (e) 1.5 M, (f) 2.0 M.

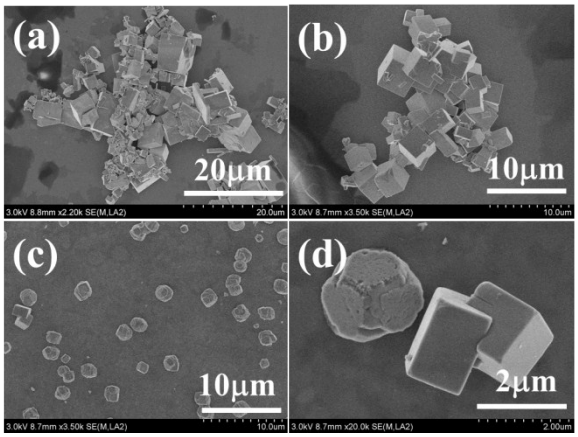

Figure S4. FE-SEM images of $NaNbO_3$ prepared at 220 °C for 16 h with NaAc (1.0 M) and different content of KOH: (a) 0.3 M, (b) 1.0 M, (c-d) 2.0 M.

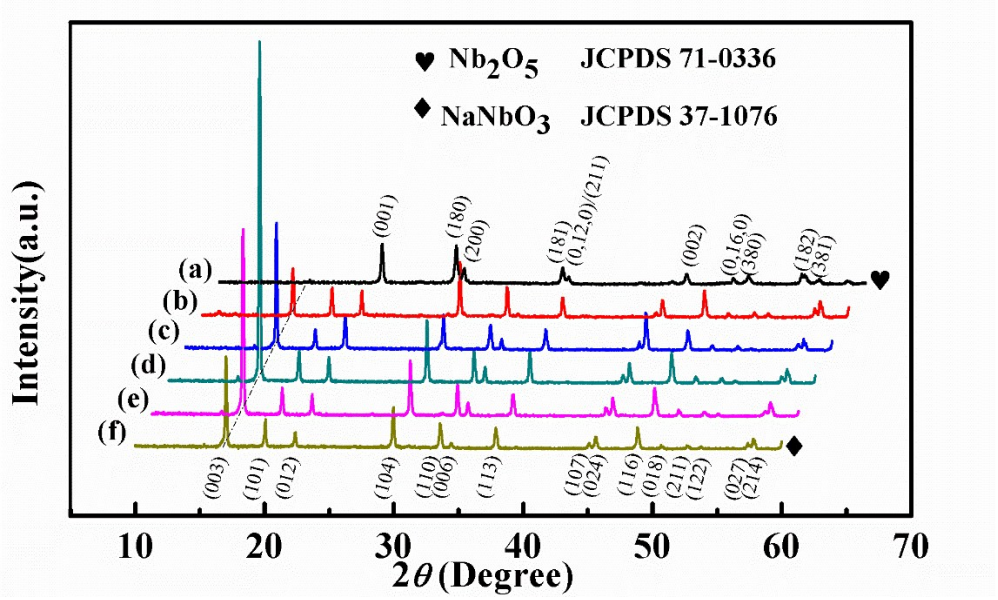

Figure S5. XRD patterns of $NaNbO_3$ prepared at 220 °C for 16 h with NaAc (0.4 M) and different content of KOH: (a) 0 M, (b) 0.3 M, (c) 0.4 M, (d) 0.5 M, (e) 0.6 M, (f) 1.0 M.

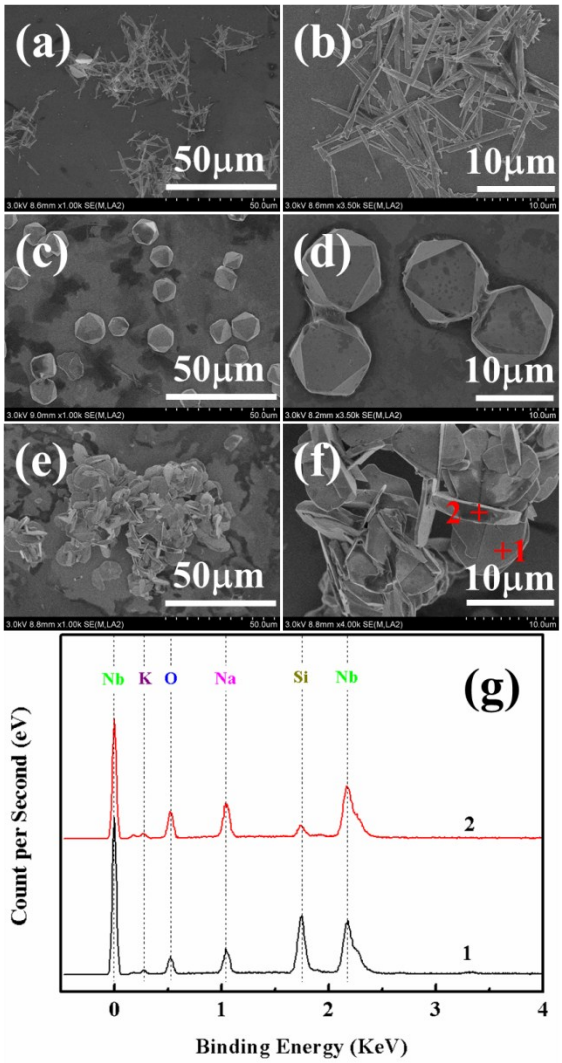

Figure S6. FE-SEM images of $NaNbO_3$ prepared at 220 °C for 16 h with NaAc (0.4 M) and different content of KOH: (a-b) 0.3 M, (c-d) 0.5 M, (e-f) 1.0 M. (g) Energy disperse X-ray spectra of the (1) top- and (2) side-surface of plate-like $NaNbO_3$ as red crosses marked in (f).

The samples obtained at 0.4M NaAc with KOH content varying from 0.3 M to 1.0 M are all attributed to rhombohedral $NaNbO_3$ (Figure S5). It's further proved that the phase structure of $NaNbO_3$ is intimately related to the content of reactant NaAc; that is higher NaAc concentration benefits the formation of orthorhombic $NaNbO_3$ while lower NaAc concentration promotes the yielding of rhombohedral $NaNbO_3$. Besides, the morphology of rhombohedral $NaNbO_3$ is quite sensitive to KOH concentration, as shown in Figure S6. The sample with 0.3 M KOH is of rod-like shape [Figure S6(a)], of which the average size is 1 μm in width and 10 μm in length, respectively. Considering that the diffraction peak intensity of samples is extremely high, which

may cover the peaks of other poor crystalized phases, it's essential to check the whole peaks carefully. In this way, it's found that some impurities emerge when KOH is 0.3 M [Figure S7(a)]. The direct characterization of the samples without pre-disperse on Si substrates shows that there coexist octahedral and rod-like shaped particles [Figure S7(b)], which is accordance to XRD results. Octahedral shaped $NaNbO_3$ with uniform size distribution of near 10 μm in edge is produced as the KOH increase to 0.5 M [Figure S6(b)]. Further increasing the KOH concentration to 1.0 M [Figure S6(c)], the shape of $NaNbO_3$ evolves to plates, of which the thickness ranges from hundreds nanometers to several micrometers, and the average width is about 10 μm. Figure S6(d) displays the elemental composition of both the side and top-surface of plate-like $NaNbO_3$, indicating that the samples are mainly composed of Na, Nb and O, while the detected K is negligible. Note that the signal of Si comes from the substrates.

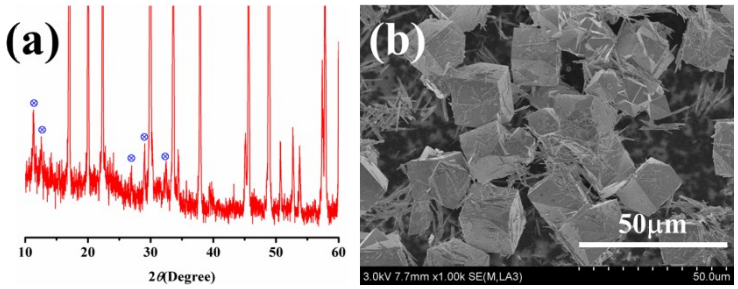

Figure S7. XRD patterns and FE-SEM of samples prepared at 220 °C for 16 h with NaAc (0.4 M) and KOH (0.3 M): (a) partial enlarged XRD pattern, where minor secondary phase attributed to $Na_7(H_3O)Nb_6O_{19}{\cdot}nH_2O$ were observed. (b) FE-SEM images observed by attaching the samples directly on the conductive paste rather than dispersing them on Si substrate.

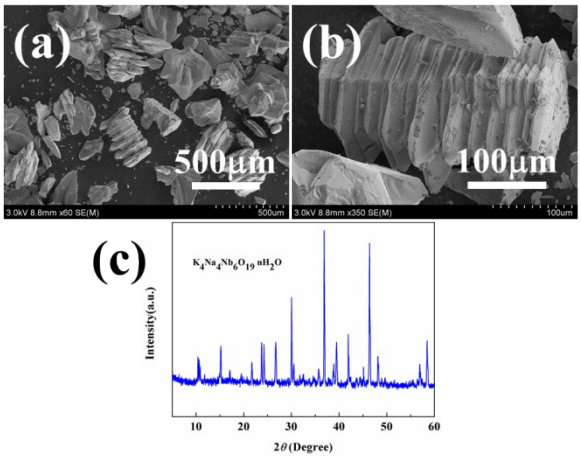

Figure S8. XRD patterns of $NaNbO_3$ prepared at (a-b) FE-SEM images and (c) XRD patterns of samples prepared at 220 °C for 16 h with KOH (2.5 M).

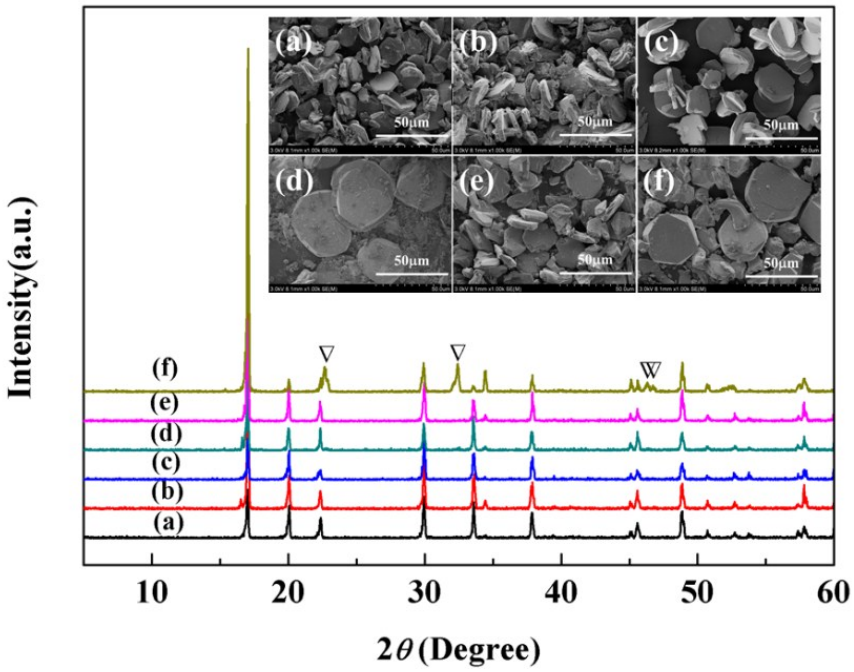

Figure S9. FE-SEM images and XRD patterns of samples prepared at 220 °C for 16 h with different sodium salts: (a) NaCl, (b) $NaNO_3$, (c) NaAc, (d) $C_2O_4Na_2$, (e) Na_2CO_3, (f) NaOH, where the concentration of Na ions and KOH was consistently kept at 0.4 M and 1.0 M, respectively.

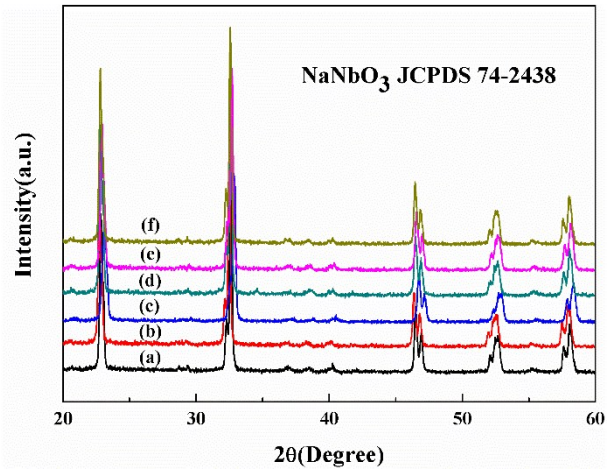

Figure S10. XRD patterns of samples prepared at 220 °C for 16 h by replace equivalent KOH with NaOH (1.0 M) and different sodium salts: (a) NaCl, (b) $NaNO_3$, (c) NaAc, (d) $C_2O_4Na_2$, (e) Na_2CO_3, (f) NaOH.

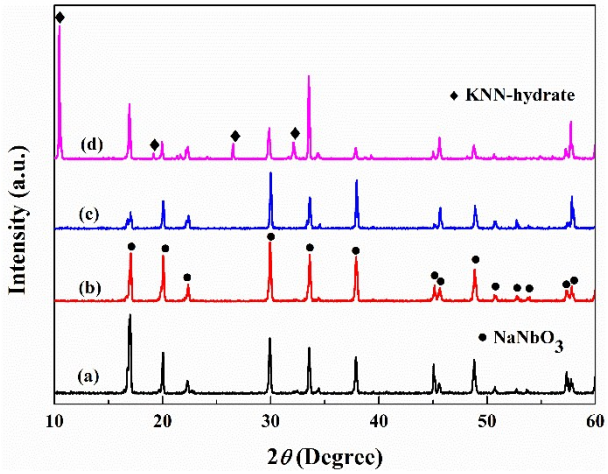

Figure S11. XRD patterns of samples prepared at 220 °C for 16 h with KOH (1.0 M), NaAc (0.4 M) and different amount of KCl: (a) 0 M, (b) 0.5 M, (c) 1.0 M, (d) 2.0 M.