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Formation of Niobates from Aqueous Peroxide Solution

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$KNbO_3$ and $LiNbO_3$ powders and thin films were fabricated through heat-treatment of their peroxide precursors prepared by the reaction of aqueous hydrogen peroxide solution with metal alkoxide. In comparison with the conventional alkoxide solution method, which is not successful for $KNbO_3$, aqueous peroxide solution method is successful for $KNbO_3$ with the advantages such as low weight loss and easy handling in preparing the niobates.

Metal alkoxide method has been well developed in preparing many functional materials in forms of thin films and ceramics.[1,2] Basically, this method includes two steps, hydrolysis and polymerization. A large quantity of research shows us the importance of the hydrolysis process in deciding the final materials. A quantitative description of the extent of hydrolysis is the hydrolysis ratio h ($h = H_2O/M(OR)_n$). By contrast to silicon alkoxides whose hydrolysis rate is easily controlled as it is slow and even requires catalysts, hydrolysis of most metal alkoxides is rapid and can lead to uncontrolled precipitation as the electronegative alkoxide groups make the metal highly prone to nucleophilic attack by water.[3–5] So there still are some simple oxides which are not successfully synthesized by metal alkoxide method, or more generally, by sol–gel method. For example, $KNbO_3$, one of important multifunctional materials with properties of optoelectronics,[6,7] ferroelectrics, and nonlinear optics, is not so successfully prepared by this method, though its chemical neighbor, $LiNbO_3$ can be easily derived from the hydrolysis of dedicately controlled alkoxide solution or completely hydrolyzed double alkoxide aqueous solution.[8–11]

Similar with the metal oxygen network with the form of M–O–M′ finally formed in metal alkoxides solution, metal peroxo group of M–O–O–M′ will form in the reaction of H_2O_2 with metal alkoxides.[12–14] In this study, aqueous metal peroxide solution was prepared as precusor. Specifically, two important functional niobates, $KNbO_3$ and $LiNbO_3$, were synthesized by heat-treatment of the peroxide precusor.

In a typical experiment, potassium or lithium ethoxide and niobium ethoxide in equivalent mol ratio were dissolved in pure ethanol to form 150 mL of 0.01 M solution, then 7 mL of 30% aq H_2O_2 solution were added with strong stirring. Keep stirring for over 2 h, then reflux at 373 K in air for several hours. In this period, distilled water was added to keep amount of the solution. After decomposing the residual H_2O_2 by platinum foil at 373 K in 3 h and condensation, 0.1 M clear solution was obtained. A part of the solution was dried into powder at 393 K in air, another part was kept for coating films. Powder and films were heat-treated at different temperatures from 623 to 1073 K in oxygen with the following heating process:

$$RT \xrightarrow{2h} PT \xrightarrow{1h} PT \xrightarrow{1h} RT$$

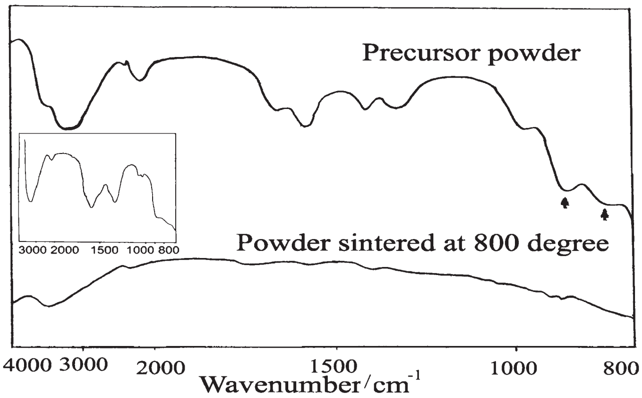

Figure 1. FT-IR spectra of $KNbO_3$ precursor powder dried at 393 K and powder after heat-treatment at 1073 K (the inset is powder dried from hydrolyzed equivalent mol ratio alkoxide solution).

Here, RT and PT are room and peak temperatures respectively.

Figure 1 shows the comparison of the FT-IR spectra of $KNbO_3$ peroxide precursor powder dried at 393 K, powder after heat-treatment at 1073 K and powder dried from hydrolyzed equivalent mol ratio alkoxide solution at 393 K. The arrows indicate the absorption of peroxide groups between 800 and 1000 cm^{-1}.[15] After heat-treatment, these peroxide groups vanished, which indicated that potassium niobium peroxide crystallized into $KNbO_3$. The peroxide absorption peaks were not observed in the alkoxide-derived powder.

Pure $KNbO_3$ and pure $LiNbO_3$ can be easily synthesized through heat-treatment their peroxide precursor in oxygen. $KNbO_3$ crystallization begins at 923 K and $LiNbO_3$ at a much lower temperature of 623 K (shown in Figure 2). Low tempera-

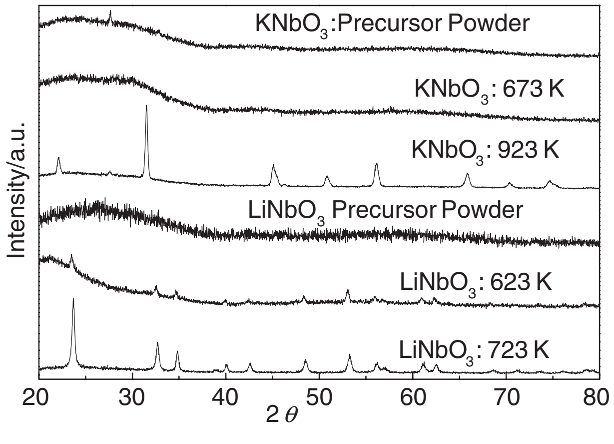

Figure 2. X-ray diffraction (XRD) patterns of $KNbO_3$ and $LiNbO_3$ powders dried from aqueous peroxide solution.

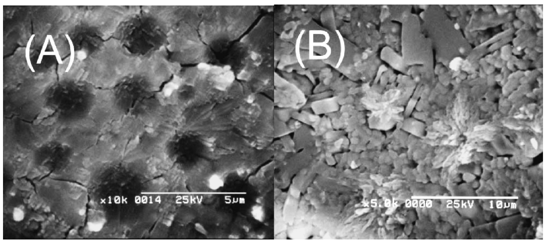

Figure 3. SEM images of $KNbO_3$ powder heat-treated at (A) 873 K (B) 1073 K.

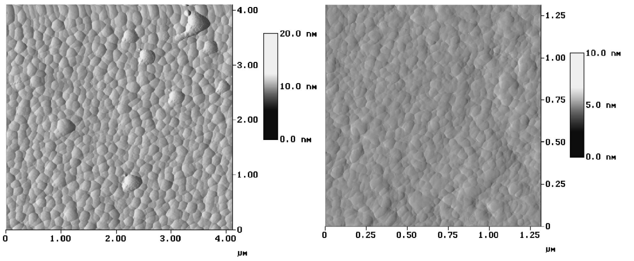

Figure 4. AFM image of the spin-coated $KNbO_3$ thin film on silicon substrate(left) and $LiNbO_3$ thin film(right) on Al_2O_3 using their precursor peroxide solution.

ture synthesis property gives advantages in fabrication of hybrid optoelectronics system.

In Figure 3, the SEM images of the powder surface give the direct evidence how the heat-treatment temperatures affect the crystallization of $KNbO_3$. After heat-treatment at 873 K, no obvious $KNbO_3$ particle was found. While after heat-treatment at 1073 K, $KNbO_3$ particles with cubic shape were observed.

These transparent aqueous metal peroxide solutions were also suitable to fabricate thin films. Figure 4 shows the surface morphology of spin-coated 100-nm-thick $KNbO_3$ film on MgO substrate after heat-treatment at 973 K and spin-coated 100-nm-thick $LiNbO_3$ film on Al_2O_3 after heat-treatment at 723 K with the same coating conditions of 3000 rpm for 20 s. Well-developed uniform grains with dimension around 150 nm can be found in $KNbO_3$ film. $LiNbO_3$ film also shows well-developed grains. No crack was found in both of these films.

Thermal analysis was done on these peroxide precursors. Figures 5 and 6 showed the comparison of thermal analysis of $KNbO_3$ and $LiNbO_3$ peroxide precursors and their alkoxide precusors dried from hydrolyzed equivalent mole alkoxide solution, respectively. The peroxide precursor shows much lower weight loss after heat-treatment. During heating from 298 to 973 K, weight loss for $KNbO_3$ peroxide is 15.6%, while it is 18.5% for the alkoxide precursor. Similarly for $LiNbO_3$, its peroxide precursor show 3.4% lower weight loss than the alkoxide precursor. The low weight loss property is favorable for coating thin films with high quality in terms of reducing cracks.

The conventional alkoxide method is not so successful in fabrication $KNbO_3$ powder and thin film. Though it is successful for $LiNbO_3$, the operation is not so simple as this peroxide method. So the most advantage of the peroxide as the precursor for niobates is easy handling as well as low weight loss and low heat-treatment temperature. The metal peroxide is a promising precursor not only for niobates, but also potentially for other oxides.

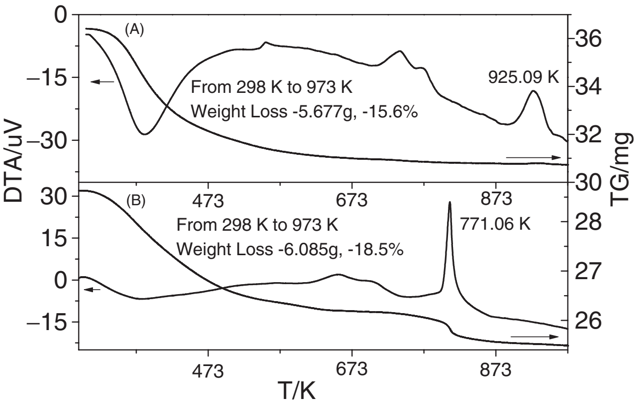

Figure 5. TG and DTA analyses of the powders dried from $KNbO_3$ peroxide solution(A) and water-hydrolyzed equivalent mole $KNbO_3$ alkoxide solution(B) in air, heating rate is 8/min.

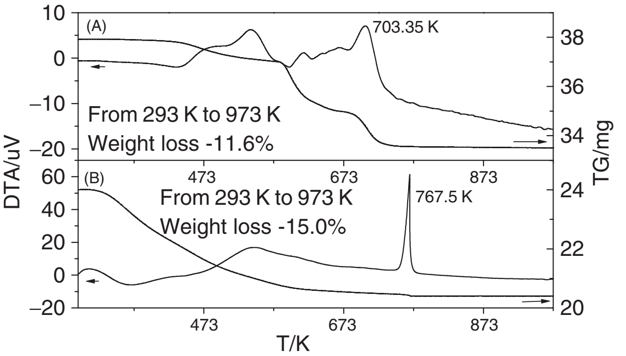

Figure 6. TG and DTA analyses of the powders dried from $LiNbO_3$ peroxide solution(A) and water-hydrolyzed equivalent mole $LiNbO_3$ alkoxide solution(B) in air, heating rate is 8/min.

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