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The atomic level journey from aqueous polyoxometalate to metal oxide



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ABSTRACT

Aqueous precursors tailored for the deposition of thin film materials are desirable for sustainable, simple, low energy production of advanced materials. Yet the simple practice of using aqueous precursors is complicated by the multitude of interactions that occur between ions and water during dehydration. Here we use lithium polyoxoniobate salts to investigate the fundamental interactions in the transition from precursor cluster to oxide film. Small-angle X-ray scattering of solutions, total X-ray scattering of intermediate gels, and morphological and structural characterization of the lithium niobate thin films reveal the atomic level transitions between these states. The studies show that (1) lithium- $[\text{H}_2\text{Nb}_6\text{O}_{19}]^{6-}$ has drastically different solution behaviour than lithium- $[\text{Nb}_6\text{O}_{19}]^{8-}$, linked to the precursor salt structure (2) in both compositions, the intermediate gel preserves the polyoxoniobate clusters and show similar local order and (3) the morphology and phases of deposited films reflect the ions behaviour throughout the journey from cluster solution to metal oxide.

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1. Introduction

Aqueous precursor chemistries for functional metal oxide coatings are generating considerable excitement with the goal of sustainable, green processes for advanced technology materials [1–4]. While there are disparate examples of thin film coatings grown from aqueous cluster precursor solutions, detailed studies of the crucial chemical and physical states of the process, and the sequential transitions between these states has not been studied. Here we investigate the transition of aqueous lithium polyoxoniobate clusters to lithium niobate thin films as a benchmark study to delineate important features of the processes that may be universal in analogous aqueous cluster precursor chemistries.

Effective metal-oxo cluster precursors possess some degree of connectivity to the film ions, which decreases the energetic barrier for self-assembly and crystallization of the coating material; and they contain minimal species that would be considered impurities in the film, such as organic ligands or charge-balancing ions. Moreover, these aqueous cluster chemistries provide superior control over composition and morphology compared to precursor chemistries of simple ions or small molecules [5–8]. Additionally,

they have produced nanocomposites that could not be obtained otherwise [9–12]. The fundamental steps of growing thin film materials from aqueous cluster precursors are illustrated generically in Fig. 1.

Alkali niobate and tantalate thin films are important in advanced technologies [13–19] and serve as an excellent case study for understanding the direct influence of aqueous precursor chemistry on thin film growth. These chemical systems are of particular interest to the current study because the polyoxometalate Lindqvist ion $[\text{M}_6\text{O}_{19}]^{8-}$ ($M = \text{Nb}, \text{Ta}$) can be made as a salt of any alkali (Li, Na, K, Rb and Cs) with excellent water-solubility [20–22]. Therefore, the unique situation is exploited in which the aqueous cluster counterion is also an integral part of the film chemistry. Although the alkali Lindqvist ion salts have been utilized as precursors for alkali niobate and alkali tantalate powders [23–29], they surprisingly have not been used to grow films from solution.

Here we specifically address the $\text{Li}^+ - [\text{Nb}_6\text{O}_{19}]^{8-}$ precursor chemistry for lithium niobate films. In 2007, Ono and Hirano [30] reported using alkoxide-derived, water-soluble Li-Nb-O-OH and Li-K-Nb-O-OH precursors for solution deposition of LiNbO_3 . While these solutions may have contained some derivative of the Lindqvist ion salts, they were neither described as such, nor were details about their structure or solution state reported. We present herein two paths from aqueous cluster precursor solution, to deposited amorphous gel, to metal oxide film, using $\text{Li}_8[\text{Nb}_6\text{O}_{19}] \cdot x\text{H}_2\text{O}$ and $\text{Li}_6[\text{H}_2\text{Nb}_6\text{O}_{19}] \cdot x\text{H}_2\text{O}$ precursors, respectively. Major

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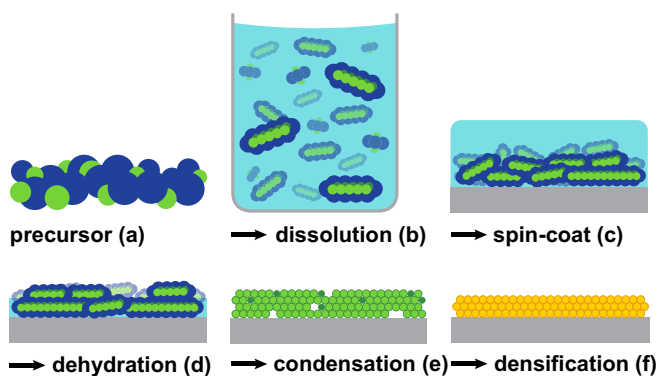


Fig. 1. Schematic showing stepwise transformation from precursor cluster solid (a) to final thin film product (f). Intermediate states are: dissolved precursor cluster (b), solution dropped onto substrate (c), rapid dehydration via spinning (d), further dehydration and condensation via low temperature heating (e) and formation of metal oxide phase via annealing (f).

characterization methods included small angle X-ray scattering (SAXS) of aqueous precursor solutions; and total X-ray scattering of the intermediate gels from the room temperature amorphous state up to the crystalline state. On a rudimentary level, composition was expected to be the most important controlling factor of the transition from precursor to thin film coating. However we have learned through this study that acid–base and ion-association chemistries of the aqueous and gel systems also significantly affect the key processes in this atom-level journey.

2. Experimental

2.1. Preparation of lithium hexaniobate

$\text{Li}_8[\text{Nb}_6\text{O}_{19}] \cdot 15.5\text{H}_2\text{O}$ (Li8): Lithium hexaniobate, $\text{Li}_8[\text{Nb}_6\text{O}_{19}] \cdot 15.5\text{H}_2\text{O}$ (FW 1169.61), was synthesized by a method similar to that which we reported prior, which is essentially an ion-exchange of K^+ for Li^+ [21]. Briefly, 5 g of $\text{K}_8[\text{Nb}_6\text{O}_{19}] \cdot x\text{H}_2\text{O}$ (synthesis reported prior) [22], which is highly soluble, is dissolved in a minimal amount of water. One liter of 1 M LiOH solution is prepared in a large beaker. While stirring, the highly concentrated $\text{K}_8[\text{Nb}_6\text{O}_{19}] \cdot x\text{H}_2\text{O}$ solution is added rapidly to the LiOH solution via pipette. Upon halting the stirring; within a minute, the solution begins to cloud as microcrystals of less soluble lithium hexaniobate grow. The beaker is left for two days to allow full crystallization and settling. The crystals are collected by decanting the clear solution, centrifugation of the collected crystals and some mother liquor, and washing with methanol to rid of excess lithium and potassium hydroxide. Energy Dispersive Spectroscopy coupled with Scanning Electron Microscopy was used to confirm there was no K^+ present in the prepared salt. If potassium is detected, the clusters are recrystallized from 1 M LiOH solution again, and usually a second crystallization will rid of all K^+ . Compositional analysis (wt%): theoretical (experimental) Nb: 46.6(48.1), Li: 4.69(4.68) A typical solution prepared with Li8 had a pH of 12.0. Li8 crystallizes as suitable size and quality for single-crystal X-ray diffraction. A crystal was selected for single-crystal analysis; see Supporting information.

$\text{Li}_6[\text{H}_2\text{Nb}_6\text{O}_{19}] \cdot 14\text{H}_2\text{O}$ (Li6): (FW 1155.73) An aqueous solution of 0.2 g $\text{Li}_6[\text{H}_2\text{Nb}_6\text{O}_{19}] \cdot 14\text{H}_2\text{O}$ in 40 ml H_2O was acidified from pH 11.8 to 11.0 by 0.1 M HCl. Then, 120 ml isopropanol was added into that solution to form a cloudy solution which was centrifuged for 1 h. The obtained solid was collected, washed by isopropanol for three times and air dried at room temperature. Yield: 0.16 g. Compositional analysis (wt%): theoretical (experimental) Nb: 48.3(47.7), Li: 3.58(3.75) A typical solution prepared with Li6 had a pH of

10.9. Li6 never produces crystals sufficient for single-crystal analysis; rather they were characterized by powder diffraction, see Supporting information. This is pertinent to later discussion on film morphology.

2.2. Aqueous cluster solution studies

Small-angle X-ray scattering data were collected on an Anton Paar SAXSess instrument with $\text{Cu-K}\alpha$ radiation and slit collimation in the q -range of $\sim 0.1\text{--}7\text{ nm}^{-1}$. Solutions of Li8 and Li6 were prepared by dissolution of the pure crystalline (Li8) and microcrystalline (Li6) powders isolated as described in prior Section 2.1 for a variety of concentrations ranging from 2.4 to 60 mM in H_2O solution and contained in a reusable 1.5 mm diameter quartz capillary tube for SAXS measurements. To ensure consistency between solutions, the most concentrated solution was prepared first, and less concentrated solutions were obtained by dilution of these solutions. Scattering was measured for 30 min or 1 h. After background subtraction and desmearing, the data were analyzed to determine size, size distribution, structure factors and PDDF (pair distance distribution function) using the IRENA macros [31] within IGOR Pro.

2.3. Intermediate gel state studies

2.3.1. Preparation of glassy Li6 and glassy Li8

Saturated aqueous solutions ($\sim 70\text{ mM}$) of Li6 and Li8 were separately prepared by dissolving in water and syringe-filtering ($0.2\text{ }\mu\text{m}$ pores). The filtered solution was placed in a 40 ml beaker, and set in a fumehood for rapid evaporation. The resulting powders were a glassy form, confirmed amorphous by X-ray diffraction. These samples, along with microcrystalline Li6, were used for total X-ray scattering studies. Thermal analysis was performed with a TA Instruments Q600 for thermogravimetric under nitrogen flow with a heating rate of $10\text{ }^\circ\text{C}/\text{min}$.

2.3.2. Total X-ray scattering studies

Total X-ray scattering data on glassy Li6, glassy Li8 and crystalline Li6 were collected at the Advanced Photon Source, beamline 11-ID-B. Samples were prepared by grinding and packing powders into a kapton capillary and then encasing in a quartz capillary to ensure rigidity upon heating. These prepared samples were then mounted in a custom resistive element furnace and nitrogen gas was flowed over the sample during heating. Data was collected at one minute increments with a ramp rate of $10\text{ }^\circ\text{C}/\text{min}$ and a wavelength of $\lambda = 0.2114\text{ \AA}$.

Phase purity of the lithium niobate was confirmed using Topas Academic [32] to fit a simulated diffraction pattern to the crystallized Li6. To analyse the total scattering data, the collected CCD data was processed using a custom script utilizing Fit2d [33] and pdfgetx3 [34]. Fit2d was calibrated against cerium dioxide and used to convert raw CCD data from the 2D area detector for the sample and background to 1D data as a function of Q . Pdfgetx3 was used to subtract the background, perform instrument and sample corrections, and obtain the structure function, $S(Q)$. The $S(Q)$ was converted to the PDF through a fourier transform according to $G(r) = 2/\pi \int Q[S(Q) - 1] \sin(Qr) dQ$ with a Q_{max} value of 28 \AA^{-1} .

Experimental PDF data of the crystallized LiNbO_3 was fit using PDFGui [35] and a good match between the two was achieved, demonstrating that the cluster transitioned completely to lithium niobate in its standard ferroelectric arrangement.

2.4. Thin film preparation and characterization

Prior to deposition, all substrates (sapphire 001 and silicon-001) were rinsed with H_2O , acetone and isopropanol, followed by a 10 min ash in an O_2 plasma. For standard characterization,

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