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Rapid Microwave-Assisted Grafting of Layered Perovskites with *n*-Alcohols

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Supporting Information

ABSTRACT: Dion−Jacobson layered niobates have been extensively researched in recent years because of a variety of useful properties such as dielectric behavior, proton conduction, and solid acid catalysis. The behavior of these materials is strongly dependent on the elemental composition and, more specifically, the interlayer surface environment. A novel method of partial grafting of *n*-alcohols into the interlayer of $HSr_2Nb_3O_{10}$ with approximately 40% conversion has been developed using microwave irradiation to generate high temperatures. This method has reduced the grafting reaction time by more than 97% while maintaining conversion rates consistent with previous methods.

Layered perovskites have shown excellent promise in the areas of ion conduction, superconduction, photocatalysis, and solid acid catalysis, to name a few.[1−4] Effective catalytic behavior in these compounds requires access to the protonated environments typically done through exfoliation into single nanosheets.[4] Sugahara et al.[5−10] has pioneered grafting techniques for the attachment of various organic groups into the interlayer of layered perovskites. In particular, Sugahara et al. have demonstrated a grafting technique for protonated Dion−Jacobson perovskites to produce derivatives with *n*-alcohols up to chain length $n = 18$. Current grafting methods of layered perovskites involve high-pressure heating at 80−150 °C for days to weeks depending on the alcohol involved. The long reaction time involved inhibits the ability to study alkoxylated samples in a timely fashion. In this current work, a novel microwave irradiation method (Scheme 1 and Table 1) was developed to reduce the grafting reaction time by 94−97% while maintaining coverage levels consistent with traditional heating methods. As will be discussed, grafting leads to a pillaring effect, where the interlayer space has greatly increased while potentially active protonated sites remain.

Scheme 1. Microwave Alkoxylation Reaction Steps

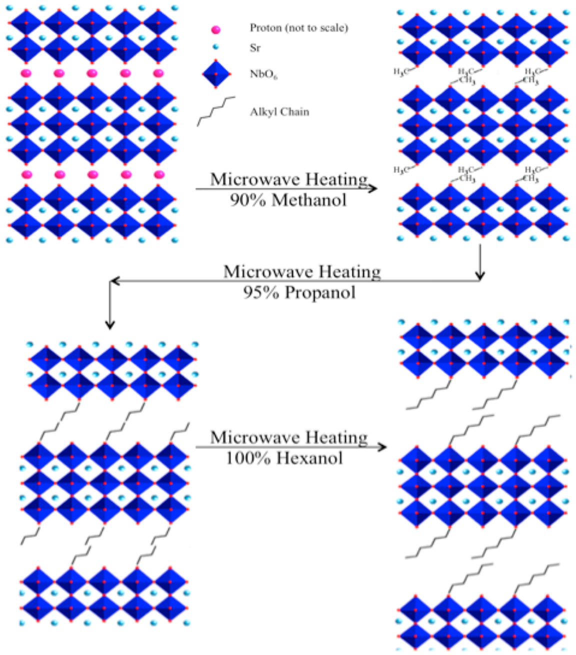

Table 1. Heating Cycles and Total Reaction Times for Microwave and Conventional Heating Methods

alcohol	heating cycle (100% power)	no. of cycles	cooling period between cycles (min)	total reaction time
methanol (microwave)	5 times (20 s on 40 s off)	10	15−20	∼4 h
methanol (conventional)	100 °C for 3 days			3 days
propanol (microwave)	5 times (40 s on 20 s off)	10	15−20	∼4 h
propanol (conventional)	150 °C for 7 days			7 days
hexanol (microwave)	4 times (60 s on 15 s off)	7	20−25	∼3.5 h
hexanol (conventional)	150 °C for 7 days			7 days

Parent compounds $RbCa_2Nb_3O_{10}$ and $RbSr_2Nb_3O_{10}$ were synthesized using molten salt heating of the carbonate and oxide precursors in RbCl salt at 800 °C for 30−45 min.[11] The hydrated protonated forms were obtained by treating samples with 6 M HNO_3 at 50 °C for 3 days. The hydrated $HSr_2Nb_3O_{10}$ samples (∼0.2 g for each sample) were then heated in a domestic microwave oven acid digestion bomb with 13.5 mL of 90% methanol using the cycled heating times shown in Table 1. Microwave heating was cycled to prevent overheating of the acid digestion bomb. After successful methoxylation, the samples were filtered, washed with acetone, and then heated in 9.5 mL of 95% *n*-propanol, followed by filtration, washing, and then heating in 10.0 mL of 100% *n*-hexanol. $HCa_2Nb_3O_{10}$ samples were grafted using the conventional heating method as

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a way of comparing the level of grafting with published reports[7] as well as with microwave alkoxylated samples. The calcium samples were heated in 90% methanol at 100 °C for 3 days in an acid digestion bomb, filtered, and washed with acetone, followed by heating in 100% *n*-propanol at 150 °C for 7 days, filtering, and washing with acetone, and finally followed by heating in 100% hexanol at 150 °C for 7 days. Powder X-ray diffraction (XRD) data were collected on a Bruker AXS D8 Focus diffractometer operated with Cu Kα radiation. ^{1}H magic-angle-spinning (MAS) Hahn Echo NMR spectra were collected at 9.4 T with a spinning rate of 10 kHz on a Varian Unity INOVA spectrometer with a ^{1}H frequency of 400 MHz. Thermogravimetric analysis (TGA) was carried out using a TA Instruments TGA Q500 thermogravimetric analyzer with a heating rate of 10 °C/min from room temperature to 800 °C under a nitrogen purge.

Powder XRD patterns were collected for 2θ ranges of 2.5–14° and 2.5–60°. The crystal structure for the compounds has an orthorhombic space group with lattice parameters a = 7.808(5) Å, b = 7.82(1) Å, and c = 32.49(2) Å for the hydrated $HSr_2Nb_3O_{10}$ phase, with the error in the last digit given in parentheses [see the Supporting Information (SI) for a detailed description of XRD pattern collection and analysis]. Upon grafting with *n*-alcohols, changes in the interlayer distance result in changes in the c lattice parameter, as shown in Figure 1. The 2.5–14° range contains reflections for the (001) and (002) planes associated with the stacking direction in the grafted and hydrated forms, respectively.

The successfully methoxylated sample showed a slight shift to a smaller stacking distance consistent with the smaller size of the methyl group compared to water molecules. The propoxylated and hexoxylated samples showed increased stacking distances from a starting point of ~16.2 Å to ~19.8 and ~24.8 Å, respectively. This significant increase in the stacking distance is consistent with the longer alkyl chains now present in the interlayer gallery. The propoxyl and hexoxyl samples' XRD patterns also show low-intensity broad reflections consistent with a small amount of hydrated phase still present. Any hydrated phase that remains in the sample is a small fraction of the final composition.

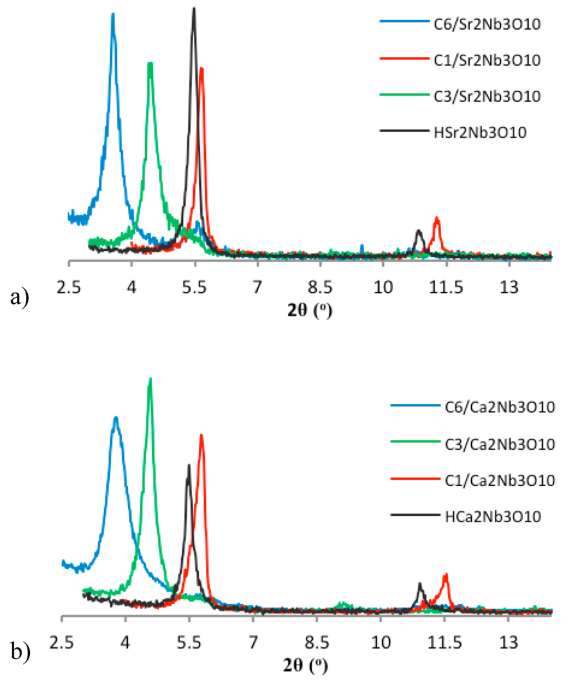

Figure 1. (a) XRD patterns for $HSr_2Nb_3O_{10}$ (black), $C1/Sr_2Nb_3O_{10}$ (red), $C3/Sr_2Nb_3O_{10}$ (green), and $C6/Sr_2Nb_3O_{10}$ (blue) synthesized using the microwave irradiation method. (b) XRD patterns for $HCa_2Nb_3O_{10}$ (black), $C1/Ca_2Nb_3O_{10}$ (red), $C3/Ca_2Nb_3O_{10}$ (green), and $C6/Ca_2Nb_3O_{10}$ (blue) synthesized using a conventional heating method.

The changing position of the stacking reflections was also seen in the $HCa_2Nb_3O_{10}$ samples grafted using conventional heating. Long-range XRD patterns were obtained for $C6/Sr_2Nb_3O_{10}$ and $C6/Ca_2Nb_3O_{10}$ (Figure S2 in the SI) to confirm that three-dimensional ordering of the compounds remained intact upon alkoxylation. Le Bail[12] fits of the long-range patterns performed with the Bruker *TOPAS* software package showed elongation of the c axis consistent with successful grafting while maintaining crystallinity in three dimensions.

While the XRD data indicate that the majority of the samples have been successfully grafted, they unfortunately do not provide quantitative information as to the alkoxyl coverage levels. To obtain quantitative information about the alkoxyl coverage, ^{1}H NMR and TGA experiments were performed on the grafted samples. MAS NMR spectra of the grafted samples contained peaks associated with the remaining water in the sample, unreacted acid sites from the Nb–O–H groups, and alkyl protons on the alkoxyl chains, as shown in Figure 2a. Peak integration of ^{1}H Hahn Echo[13] NMR spectra with varying relaxation times was used to estimate the alkoxyl coverage for each sample by comparing the integral of the unreacted acid sites to the integral of the alkyl peak, as shown in Figure 2b. Varying relaxation times were used to extrapolate back to an echo time of zero and negate the effects of differing relaxation rates. Methoxylated and propoxylated samples did not show uniform exponential decay due to a broad overlapping peak at short relaxation times, resulting in a slightly skewed data set. The ^{1}H NMR results indicate 40% coverage per perovskite unit for hexoxylated samples.

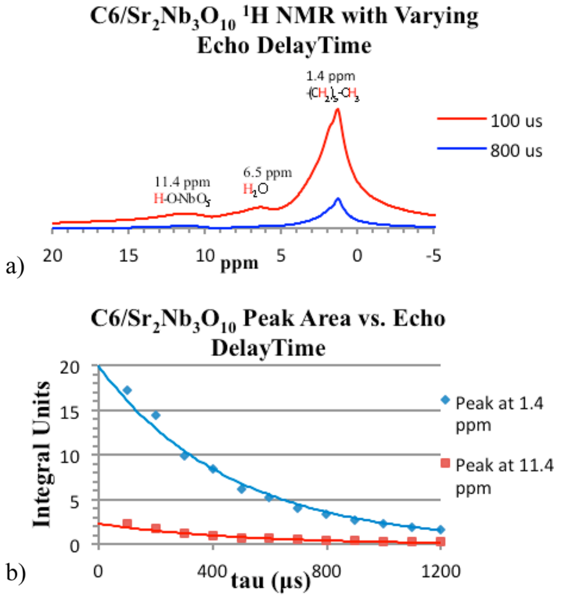

Figure 2. (a) ^{1}H MAS Hahn Echo NMR spectra for $C6/Sr_2Nb_3O_{10}$ with varying echo delay times and (b) results of peak integration as a function of the echo delay time.

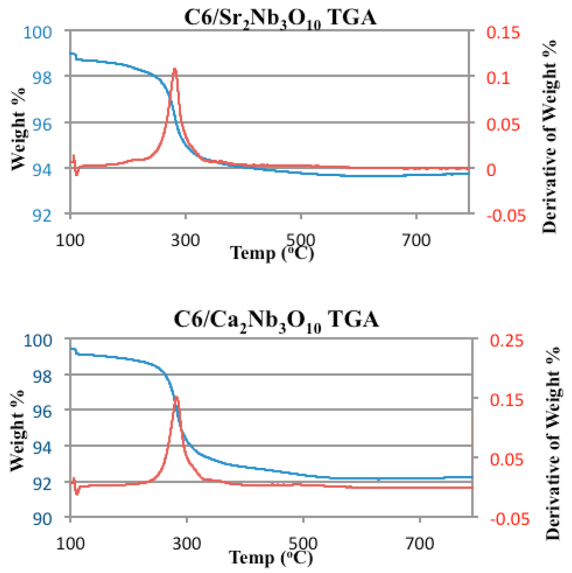

Figure 3. TGA data for C6/$Sr_2Nb_3O_{10}$ (above) and C6/$Ca_2Nb_3O_{10}$ (below) with temperatures ranging from 100 to 800 °C. On the basis of theoretical values of 11.84% and 13.84% for 100% alkoxyl coverage of the strontium and calcium samples, the alkoxyl coverage was found to be 39.1% and 45.0%, respectively.

TGA data shown in Figure 3 collected from 30−800 °C were performed to substantiate the NMR results. Water loss was seen up to 110 °C, followed by further mass loss up to 800 °C. Assuming alcohol loss would occur before condensation of the compound into a denser phase, the mass loss derivatives were used to determine the appropriate point to consider alcohol loss as complete, which was found to be approximately 375 °C. The TGA results are in good agreement with the NMR data and suggest 39.1% coverage per perovskite unit for the microwave hexoxylated samples. TGA data were also obtained for the hexoxylated C6/$Ca_2Nb_3O_{10}$ compound synthesized using conventional heating; it was found that the alkoxyl coverage was 45.0%.

Not only has the total reaction time to obtain the hexoxylated phase been decreased from 17 days to 12 h, but there is no significant decrease in the total alkoxyl group coverage of the compound. XRD, NMR, and TGA data have shown that microwave irradiation is an enticing alternative to conventional heating for alkoxylation of layered perovskites. While using longer-chain *n*-alcohols such as *n*-octadecanol is not viable because of limited microwave susceptibility, long-chain alcohols could possibly be introduced if more polar groups are present on the chain to increase the microwave susceptibility. Thorough reviews by Kappe[14] and Gabriel et al.[15] on microwave heating of organic compounds discuss in great detail the properties of molecules that affect the ability of a solvent to absorb microwave energy (referred to as the loss tangent) such as the nature of the functional groups and volume of the molecule. This should serve as an excellent resource for those looking to adopt this microwave-assisted grafting technique using other organic species.

Furthermore, the incorporation of alkyl chains into the interlayer gallery of these perovskites creates a hydrophobic environment that can potentially be treated with low-polarity solvents as a method of exfoliation into nanosheets. This novel microwave irradiation method of alkoxyl grafting should now make further research into the effects of grafting on layered perovskites significantly more viable.

■ ASSOCIATED CONTENT

Supporting Information

Detailed experimental procedure, long-range XRD patterns, and table of parameters determined by the Le Bail method. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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