

## Sol–Gel Preparation of $\text{Bi}_2\text{M}_x\text{V}_{1-x}\text{O}_{5.5-\delta}$ Films ( $\text{M} = \text{Cu}, \text{Nb}; x = 0.1, 0.3$ )

J. W. Pell,<sup>†</sup> K. M. Delak,<sup>†</sup> and H.-C. zur Loye\*<sup>‡</sup>

Department of Chemistry, Massachusetts Institute of Technology,  
Cambridge, Massachusetts 02139, and Department of Chemistry and Biochemistry,  
University of South Carolina, Columbia, South Carolina 29208

Received November 4, 1996. Revised Manuscript Received February 17, 1998

The sol–gel deposition of  $\text{Bi}_2\text{Cu}_{0.1}\text{V}_{0.9}\text{O}_{5.35}$  ( $\text{BiCuVO}_x$ ) and  $\text{Bi}_2\text{Nb}_{0.3}\text{V}_{0.7}\text{O}_{5.5}$  ( $\text{BiNbVO}_x$ ) films up to  $2\ \mu\text{m}$  thick onto quartz substrates is reported. Films of both materials can be deposited, initially crack-free, on quartz.  $\text{Bi}_2\text{Nb}_{0.3}\text{V}_{0.7}\text{O}_{5.5}$  films on quartz remain homogeneous and defect-free at all temperatures, but  $\text{Bi}_2\text{Cu}_{0.1}\text{V}_{0.9}\text{O}_{5.35}$  films develop grooves and voids between grains during thermal processing. A number of additives were tested with the  $\text{BiCuVO}_x$  precursor solutions for their effects on film morphology and were found to give no improvement in the film quality. Process temperature and alkoxide/hydrolysis water ratio were varied as well. Preliminary results for deposition of the films onto porous alumina substrates are reported.

### Introduction and Background

**Applications.** Air separators utilizing a thin, dense membrane of an oxygen ion conducting material offer significant advantages over conventional methods involving repeated fractional distillation of air, in terms of both efficiency and economics.<sup>1,2</sup> Likewise, membrane reactors incorporating an ionic conductor can increase conversion efficiency and selectivity over fully oxidized products in partial oxidation and ammonoxidation reactions relative to present reactor designs.<sup>3–7</sup> Decreasing the thickness of a membrane of the conducting material shortens the path that oxygen ions must traverse, effecting a corresponding increase in the oxygen flux at a given temperature.

An important restriction, however, is that the membrane must be crack- and pore-free and robust under thermal cycling. Recrystallization and other processes leading to film agglomeration, hillock formation, and the appearance of voids in the film have been studied for a number of physical deposition processes, but reports of these phenomena with films deposited by the sol–gel method are to our knowledge absent. There are relatively few studies of film behavior under thermal cycling.<sup>8</sup>

**Methods.** One of the most versatile techniques for producing thin films of oxide materials is the sol–gel method, which has been demonstrated to produce high-quality films of a number of materials, including yttria-stabilized zirconia (YSZ)<sup>8,9</sup> and bismuth and lead titanates.<sup>10–13</sup> In the sol–gel method, a solution of suitable precursors—commonly a mixture of metal alkoxides, carboxylates, and/or nitrates—is deposited onto a substrate, followed by gelation to a homogeneous solid layer, which is dried and fired to remove unwanted organic components.<sup>14</sup> Higher-temperature processing yields a crystalline film, and repetition of this procedure can result in films several microns in thickness. The addition of compounds that react with the precursors to change their hydrolysis behavior is often necessary to stabilize the metal oxide polymer in solution and can modify the polymer network by preventing three-dimensional cross-linking.<sup>15</sup> Such modification of the precursor network can influence the phases obtained on pyrolysis, as seen in studies of the  $\text{YBa}_2\text{Cu}_4\text{O}_8$  superconductors,<sup>16</sup> and can have dramatic effects on both the density and the morphology of a bulk mass or film made via the sol–gel method.<sup>14</sup> Finally, the precursor solution's viscosity and the parameters associated with the film deposition process partially determine the film

\* To whom all correspondence should be addressed.

<sup>†</sup> Massachusetts Institute of Technology.

<sup>‡</sup> University of South Carolina.

(1) Chen, M. S.; Hegarty, P.; Steyert, W. A. Oxygen Recovery from Turbine Exhaust Using Solid Electrolyte Membrane. U.S. Patent 5,118,395, June 2, 1992, Air Products and Chemicals, Inc.

(2) Thorogood, R. M.; Srinivasan, R.; Yee, T. F.; Drake, M. P. Composite Mixed Conductor Membranes for Producing Oxygen. U.S. Patent 5,240,480, August 31, 1993, Air Products and Chemicals, Inc.

(3) Dumelie, M.; Nowogrocki, G.; Boivin, J. C. *Solid State Ionics* **1988**, 28–30, 524.

(4) Hsieh, H. P. *Catal. Rev. Sci. Eng.* **1991**, 33, 1.

(5) Harold, M. P.; Lee, C.; Burggraaf, A. J.; Keizer, K.; Zaspalis, V. T.; de Lange, R. S. A. *MRS Bull.* **1994**, 14, 34.

(6) Minh, N. Q. *J. Am. Ceram. Soc.* **1993**, 76, 563.

(7) Rincon-Rubio, L. M.; Nguyen, B. C.; Mason, D. M. *J. Electrochem. Soc.* **1985**, 132, 2919.

(8) Kueper, T. W.; Visco, S. J.; DeJonghe, L. C. *Solid State Ionics* **1992**, 52, 251.

(9) Chen, C. C.; Nasrallah, M. M.; Anderson, H. U. *Solid State Ionics* **1994**, 70/71, 101.

(10) Joshi, P. C.; Krupanidhi, S. B. *J. Appl. Phys.* **1992**, 72, 5827.

(11) Selvaraj, U.; Prasadarao, A. V.; Komarneni, S.; Roy, R. *Mater. Lett.* **1995**, 23, 123.

(12) Toyoda, M.; Hamaji, Y.; Tomono, K.; Payne, D. A. *Jpn. J. Appl. Phys.* **1993**, 32, 4158.

(13) Yoon, D. S.; Kim, C. J.; Lee, J. S.; Choi, C. G.; Lee, W. J. *MRS Proc.* **1994**, 343, 499.

(14) Brinker, C. J.; Scherer, G. W. *Sol–Gel Science*; Academic Press: Boston, 1990.

(15) Chandler, C. D.; Roger, C.; Hampden-Smith, M. J. *Chem. Rev.* **1993**, 93, 1205.

(16) Kareiva, A.; Bryntse, I.; Karppinen, M.; Niinisto, L. *J. Solid State Chem.* **1996**, 121, 356.

thickness and its resistance to cracking. Several groups have reported the sol-gel deposition of films of YSZ on continuous and porous substrates.

**Materials.** The compound  $\text{Bi}_2\text{VO}_{5.5}$  is a member of the Aurivillius family of compounds,  $(\text{Bi}_2\text{O}_7)^{2+}(\text{A}_{n-1}\text{M}_n\text{O}_{3n+1})^{2-}$ . Its high-temperature ( $\gamma$ ) phase exhibits ionic conductivities that are among the highest known, almost 2 orders of magnitude higher than that of YSZ at these temperatures.<sup>17,18</sup> This high-temperature phase may be stabilized to room temperature by doping with a number of transition metals, yielding the  $\text{BiMVO}_x$  family of ionic conductors ( $\text{M} = \text{dopant metal}$ ),  $\text{Bi}_2\text{M}_x\text{V}_{1-x}\text{O}_{5.5-\delta}$ .<sup>18-22</sup> The solid-state synthesis of  $\text{BiMVO}_x$  materials from the metal oxides is straightforward, and a sol-gel route to the bulk undoped parent phase as well as to several of the doped compounds was recently reported by our group.<sup>23,24</sup>

Because of the apparent promise of the  $\text{BiMVO}_x$  family of compounds for use in the membrane-based applications described above, we undertook work with the ultimate aim of producing defect-free films of these compounds on porous supports. In this paper we report studies of the thermal resilience of films of these materials deposited on nonporous quartz substrates and preliminary results for films deposited on porous substrates.

## Experimental Section

Precursors were prepared and handled under an inert atmosphere. Films were cast in air at room temperature from solutions hydrolyzed with water equal to the moles of alkoxide group, except in experiments varying water.

**Preparation of Stock Precursor Solution.** Alcohol-soluble bismuth acetate,  $\text{Bi}(\text{OAc})_3$ , and vanadium(IV) 2-methoxyethoxide (V-2MOE) were prepared as described previously.<sup>23</sup> Bismuth acetate was dissolved in 2-methoxyethanol (2MOE) with gentle warming. V-2MOE and either copper(II) acetate (anhydrous, Strem, 99%) or niobium(V) isopropoxide (Alfa, [Nb] verified gravimetrically as  $\text{Nb}_2\text{O}_5$ ) were added to give the stoichiometries  $\text{Bi}_2\text{Cu}_{0.1}\text{V}_{0.9}\text{O}_{5.35}$  or  $\text{Bi}_2\text{Nb}_{0.3}\text{V}_{0.7}\text{O}_{5.5}$ , respectively. This "stock" solution was 0.05 M in  $\text{Bi}^{3+}$ . Unhydrolyzed solutions were stable indefinitely. The decomposition temperature of a hydrolyzed and dried sample of each precursor solution was checked using thermogravimetric analysis (TGA).

**Preparation of Substrates.** Quartz substrates were cleaned in 48% aqueous HF, rinsed in deionized (DI) water, and baked at 600 °C. Quartz substrates washed only in acetone and dried at 150 °C were also tested, but these films showed poor adhesion to substrates prepared in this manner, with cracking and delamination visible under low-power (150 $\times$ ) magnification. Presumably the HF serves to "scuff" the surface of the substrates, providing adhesion points for the  $\text{BiMeVO}_x$  films.<sup>8</sup>

(17) Abraham, F.; Debreuille-Gresse, M. F.; Mairesse, G.; Nowogrocki, G. *Solid State Ionics* **1988**, 28-30, 529.

(18) Kendall, K.; Navas, C.; Thomas, J. K.; zur Loye, H.-C. *Chem. Mater.* **1996**, 8, 642.

(19) Sharma, V.; Shukla, A. K.; Gopalakrishnan, J. *Solid State Ionics* **1992**, 58, 359.

(20) Tuller, H. L.; Moon, P. K. *Mater. Sci. Eng. B-Solid State* **1988**, B1, 171.

(21) Vannier, R. N.; Mairesse, G.; Abraham, F.; Nowogrocki, G. *J. Solid State Chem.* **1993**, 103, 441.

(22) Abraham, F.; Boivin, J. C.; Mairesse, G.; Nowogrocki, G. *Solid State Ionics* **1990**, 40/41, 934.

(23) Pell, J. W.; Ying, J. Y.; zur Loye, H. C. *Mater. Lett.* **1995**, 25, 157.

(24) Pell, J. W.; Delak, K. M.; zur Loye, H.-C. Sol-gel Route to Oxygen Ion Conductors in Thin Film Form. In *Polycrystalline Thin Films: Structure, Texture, Properties, and Applications II*; MRS Symposium Proceedings; Frost, H. J., Ross, C. A., Parker, M. A., Holm, E. A., Eds.; 1996; Vol. 403, p 459.

Anopore brand (Whatman) porous alumina filter disks (0.02  $\mu\text{m}$  pore size) were cleaned in aqua regia, rinsed with water and acetone, and heated to 650 °C to remove detergents or other organics that may have been used in their manufacture. The filter disks measured 50-60  $\mu\text{m}$  in thickness.

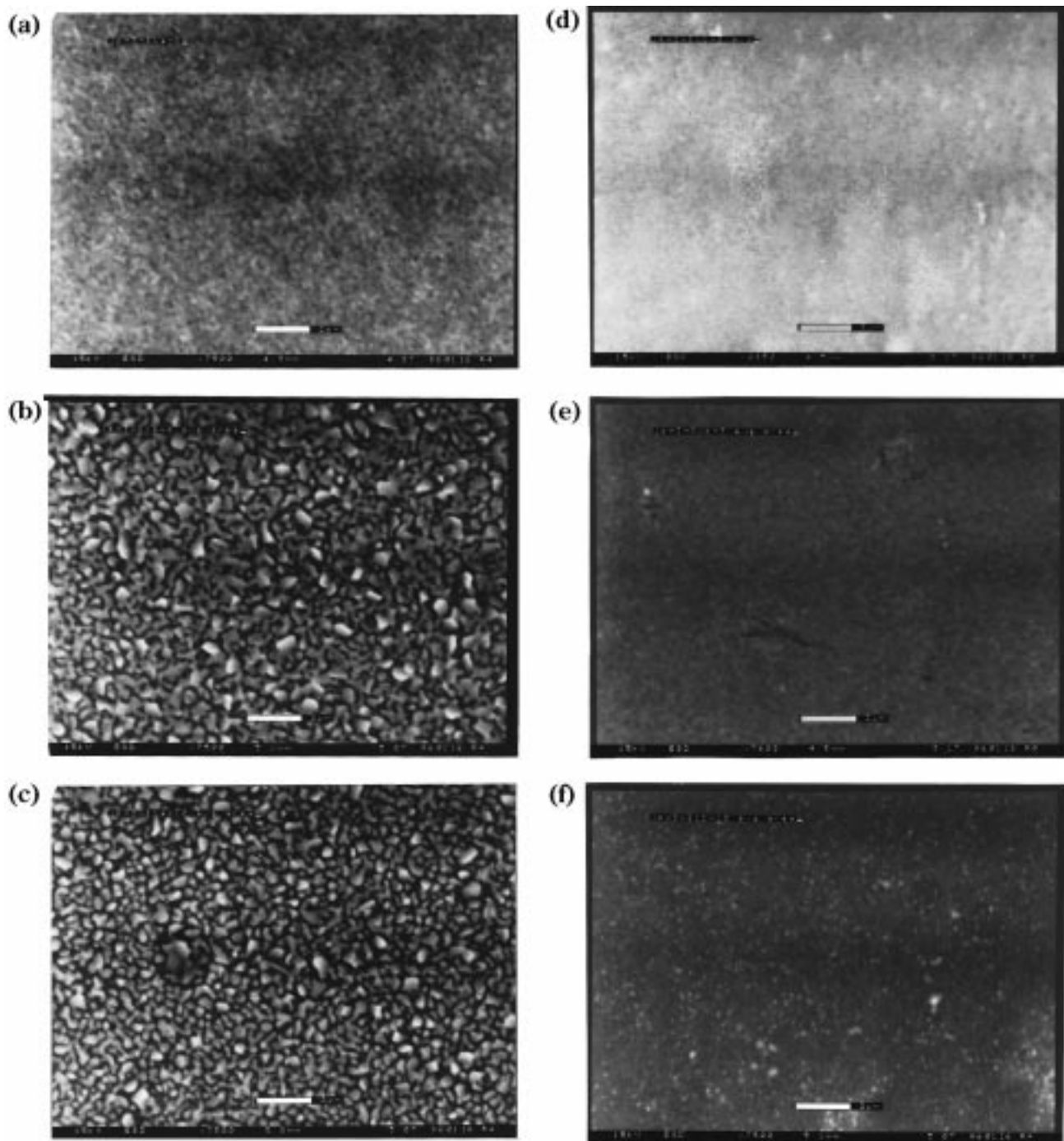
**Film Casting and Characterization.** Films were cast by placing a drop of hydrolyzed precursor solution onto a quartz substrate or Anopore disk, which was spun at 7500 rpm for 5 s. A portion of each substrate was masked to create a step for profilometry. Samples were heated on a hotplate (approximately 350 °C) for 2 min and then inserted into a preheated furnace (450 °C) for 15 min. This process was repeated to build up 10 layers of oxide film. Final annealing times and temperatures are indicated in each section below. Samples were characterized by grazing incidence X-ray diffraction (GIXRD, Siemens D5000 with grazing incidence attachment) at incident angles of 0.75-1.5°, profilometry (Dektak, 12.5- $\mu\text{m}$  stylus), and environmental scanning electron microscopy (ESEM). Approximately 50 Å of gold was evaporated onto samples before microscopy to improve imaging.

**Process Conditions.** Some process conditions were varied to show the effect on the morphology and the general quality of the resulting film. (a) Variation of hydrolysis water. The ratio ( $W$ ) of hydrolysis water to alkoxide groups present was varied from  $W = 0$  to 5. (b) Variation of heating temperature. After deposition of 10 film layers, the sample was heated in air at 450-850 °C for 2 h, with cooling at 2 °C/min. (c) Variation of additives. Aliquots of each of the stock solutions were diluted 50% with anhydrous methanol, and 1 of the following was added in a ratio of one mole of additive per mole of alkoxide groups present: ethanolamine (EA), diethanolamine (DEA), triethanolamine (TEA), *N,N*-dimethylformamide (DMF), ethylene glycol (EG), 1,3-propanediol (PD), or acetic acid (Ac). A milky precipitate was noted in some of the EA samples, and these solutions were discarded. One sample for each dopant was left additive-free as a control. All solutions were normalized to the same concentration by addition of 2MOE. Each of the resulting precursor solutions was hydrolyzed with deionized water in an amount equivalent to the moles of alkoxide groups present ( $W = 1$ ). Hydrolyzed solutions were stable for months. After deposition of 10 layers of film, samples were heated in air at 550 °C for 2 h, with cooling at 2 °C/min. (d) Porous substrates. Five layers of  $\text{BiCuVO}_x$  film were deposited onto an Anopore disk for each additive-containing precursor solution, with heating between each layer as described. The final annealing step involved heating in air at 550 °C for 4 h, with cooling at 2 °C/min.

## Results

TGA of the hydrolyzed and dried gels demonstrated that decomposition was complete by 375 °C, with an approximate TGA mass loss of less than 10%. XRD of bulk materials showed the formation of the desired  $\text{BiMVO}_x$  phase by 450 °C;<sup>24</sup> therefore, this was the lowest temperature to which film samples were heated in any experiment. Films which showed essentially no cracks by electron microscopy were transparent. The color varied according to the film thickness and the angle of viewing, with films in excess of 1.5  $\mu\text{m}$  in thickness having a deep yellow-orange color similar to that of the bulk material. Conversely, very poor quality films were conversely, cloudy or opaque to the naked eye, and cracking or delamination could be seen under low power through an optical microscope (150 $\times$ ).

**Varying Annealing Temperature.**  $\text{BiCuVO}_x$  precursor solutions containing no additives were spin-cast onto cleaned quartz substrates and, after 10 layers cast and heated as described above, annealed at 450, 550, and 650 °C.  $\text{BiCuVO}_x$  films annealed at 450 °C were homogeneous and defect-free, but those heated at 550-



**Figure 1.** Effects of annealing temperature. (a–c)  $\text{BiCuVO}_x$  films on quartz showing increasing agglomeration with annealing temperature: (a) 450 °C, (b) 550 °C, and (c) 650 °C. (d–f)  $\text{BiNbVO}_x$  films on quartz. Note the general smoothness compared with the  $\text{BiCuVO}_x$  films: (d) 450 °C, (e) 550 °C, and (f) 650 °C. Scale bars in panels a–c, e, and f are 2  $\mu\text{m}$ ; in panel d, 5  $\mu\text{m}$ .

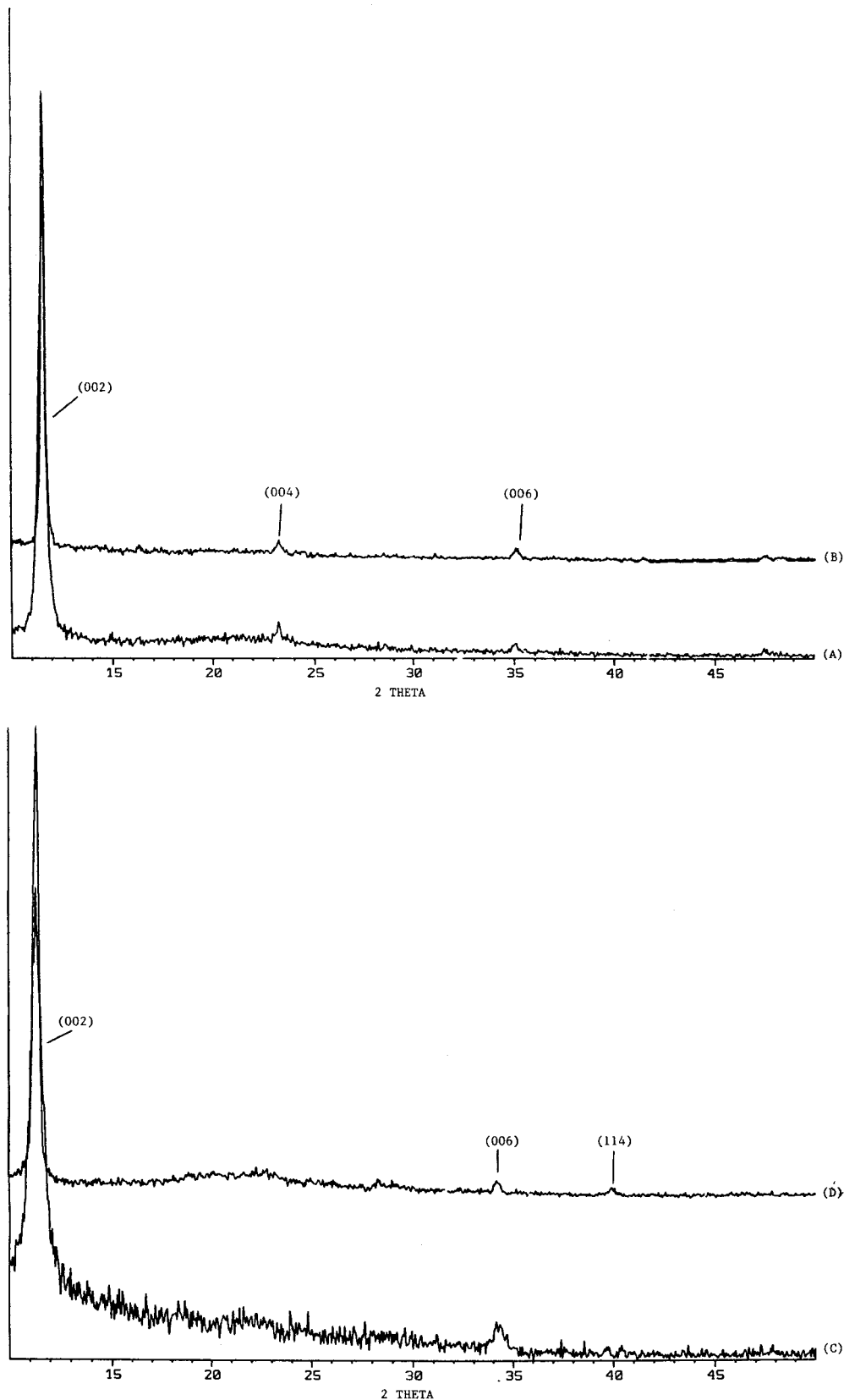
850 °C exhibited grain formation with the appearance of voids (Figure 1). GIXRD showed the formation of the desired phase at 450 °C; crystallinity and a strong 00 $l$ -texturing both developed further with increasing firing temperature (Figure 2). Films heated to 875 °C demonstrated a drastic loss of crystallinity according to GIXRD, with the ingrowth of unidentified new peaks. TGA/DTA data on bulk  $\text{BiCuVO}_x$  indicates that melting occurs at 895 °C without evidence of decomposition or loss of material prior to this temperature.

$\text{BiNbVO}_x$  precursor solutions containing no additives were similarly spin-cast onto quartz substrates. Those heat-treated at 450 °C were homogeneous and defect-free, and GIXRD showed the desired  $\text{Bi}_2\text{Nb}_{0.3}\text{V}_{0.7}\text{O}_{5.5}$

phase, with preferred 00 $l$ -orientation. These films, contrary to what was observed with  $\text{BiCuVO}_x$  films, remained homogeneous, phase-pure, and mainly defect-free according to ESEM (some defects could be traced to dust contamination) to the highest heating temperature of 650 °C (compare Figures 1 and 2).

*Variation of Hydrolysis Ratio.* Unhydrolyzed solutions would not wet the substrates, due to the poor rheological properties of these solutions, and the GIXRD patterns for these films showed formation of  $\text{BiVO}_4$  and  $\text{Bi}_2\text{O}_3$  in addition to the desired  $\text{Bi}_2\text{Cu}_{0.1}\text{V}_{0.9}\text{O}_{5.35}$  phase. Among  $\text{BiCuVO}_x$  films cast from precursor solutions hydrolyzed with water/alkoxide ratios equal to and greater than 1, there was no difference in film morphol-



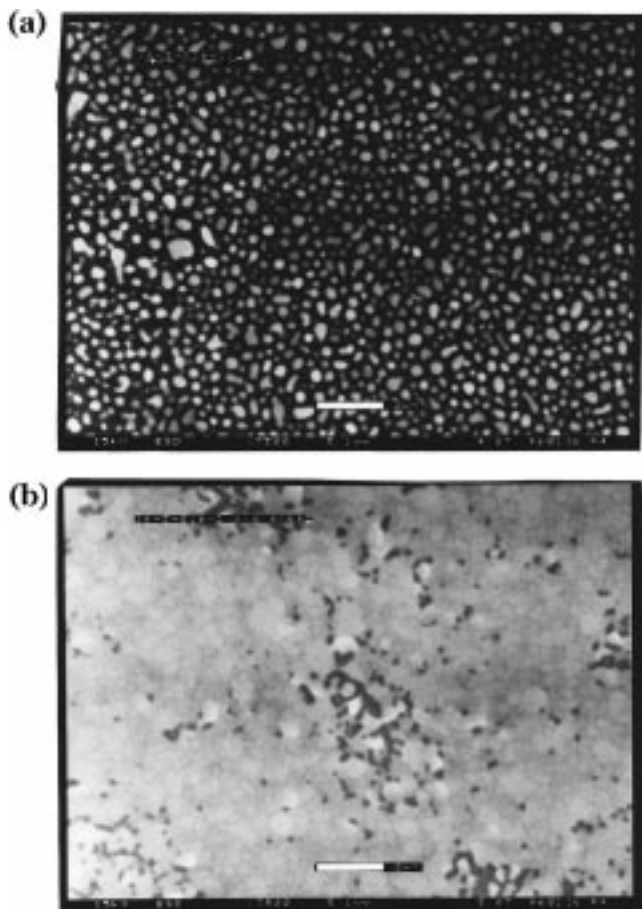


**Figure 2.** GIXRD patterns of films. Incident angle,  $1^\circ$ . Note the high degree of 00 $l$ -orientation. (a, b)  $\text{BiCuVO}_x$ , 450 and 650  $^\circ\text{C}$ . (c, d)  $\text{BiNbVO}_x$ , 450 and 650  $^\circ\text{C}$ .

ogy for any annealing temperature.

*Films from Precursors Containing Additives.*  $\text{BiCuVO}_x$  films made from precursor solutions with added 1,3-propanediol (PD), *N,N*-dimethylformamide (DMF), acetic acid (Ac), ethylene glycol (EG), triethanolamine

(TEA), or diethanolamine (DEA) were cast as described above and annealed at 550  $^\circ\text{C}$ . These films showed agglomeration or dewetting which is in some cases worse than that in the controls. A variation in the appearance of the  $\text{BiCuVO}_x$  grains or islands with the



**Figure 3.** Examples of the effects of additives in the  $\text{BiCuVO}_x$  precursor solution: (a) 1,3-propanediol and (b) diethanolamine. Scale bars are 2  $\mu\text{m}$ .

identity of the additive was noted: the amount of substrate surface lacking ceramic film coverage decreased as the identity of the additive changed, in the order  $\text{PD} > \text{EG} > \text{DMF} > \text{Ac} > \text{DEA}$  (Figure 3). GIXRD revealed that all the films were strongly 001-oriented. Films made from precursor solutions containing TEA showed a mixture of  $\text{BiCuVO}_x$  and  $\text{BiVO}_4$  phases, but all other GIXRD patterns showed the formation of phase-pure  $\text{BiCuVO}_x$ . The film thickness was 0.8–1.4  $\mu\text{m}$  by profilometry (10 layers). On the other hand,  $\text{BiNbVO}_x$  films demonstrated little variation in quality with precursor additive, and all except TEA showed formation of 001-oriented and phase-pure  $\text{BiNbVO}_x$  by GIXRD. As with  $\text{BiCuVO}_x$ , the TEA-containing precursor solution gave films which were blotchy and inhomogeneous; GIXRD of these films showed a mixture of  $\text{BiNbVO}_x$  and  $\text{BiVO}_4$ .

Solutions of 0.02 M [V-2MOE] in 2MOE were prepared and 1 mole equivalent of additive per mole of alkoxide group was added. ( $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were dominated by the solvent and additive peaks and were therefore uninformative. Nonalcoholic solvents would not dissolve the bismuth acetate, and alcoholic solvents other than 2MOE can be expected to exchange for 2MOE in the vanadium coordination sphere.)  $^{51}\text{V}$  NMR data is given in Table 1.

**Porous Substrates.** Preliminary attempts were made to deposit films of  $\text{BiCuVO}_x$  and  $\text{BiNbVO}_x$  on porous alumina substrates, with an annealing temperature of 550  $^\circ\text{C}$ . The results seen with both materials were

**Table 1**

precursor soln <sup>a</sup>	$^{51}\text{V}$ NMR peaks (ppm, $\text{VOCl}_3$ , $\delta = 0$ )
V-2MOE	-544
V-2MOE + $\text{Bi}(\text{OAc})_3$	-541
V-2MOE + DEA	-437, -461
V-2MOE + EG	-471, -479, -540
V-2MOE + DMF	-545
V-2MOE + MeOH	-532
V-2MOE + AcH	-521

<sup>a</sup> [V] in 2MOE =  $2.2 \times 10^{-3}$  M; additive =  $6.5 \times 10^{-3}$  M. DEA = diethanolamine; EG = ethylene glycol; DMF = *N,N*-dimethylformamide; MeOH = methanol; AcH = acetic acid.

**Table 2**

additive <sup>a</sup>	film quality
DMF	pore-free
PD	pore-free
EG	cracking and pores
none	pore-free
AcH	cracking and pores
DEA	pore-free
TEA	pores visible

<sup>a</sup> TEA = triethanolamine; DEA = diethanolamine; EG = ethylene glycol; DMF = *N,N*-dimethylformamide; MeOH = methanol; PD = 1,3-propanediol; AcH = acetic acid.

essentially identical. Precursor solutions containing no additive or containing the additives DMF, PD, and DEA gave homogeneous, pore-free films (Table 2). (Some pinholes due to dust contamination could be seen in some samples; the area around these holes was uncracked, however, showing a certain degree of elasticity in the film (Figures 3–5).) Solutions containing acetic acid, ethylene glycol, or triethanolamine gave poor-quality films. The rough topography of the defect-free films reflects the texture of the substrate. The results from GIXRD of the films on porous substrates were inconclusive, as the diffraction patterns were dominated by signal from the porous alumina substrates.

## Discussion

**General Behavior.** Initially, films of both  $\text{BiCuVO}_x$  and  $\text{BiNbVO}_x$  were homogeneous and defect-free to ESEM inspection. However, while  $\text{BiNbVO}_x$  films remained defect-free to annealing temperatures of 650  $^\circ\text{C}$ , grain growth in  $\text{BiCuVO}_x$  films annealed at 550  $^\circ\text{C}$  resulted in hillock and void formation, with annealing temperatures  $> 650$   $^\circ\text{C}$  leading to severe film agglomeration (Figure 1c). Similar grain growth has been seen in films of  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ , though void formation was not reported.<sup>25</sup>

While there are numerous reports in the literature regarding the phenomena of grain growth, hillock and void formation, and film agglomeration for films grown by physical deposition techniques,<sup>26–29</sup> we have seen no corresponding comments on sol-gel films. Several reports of the behavior of sol-gel films on thermal cycling have focused on cracking due to thermal

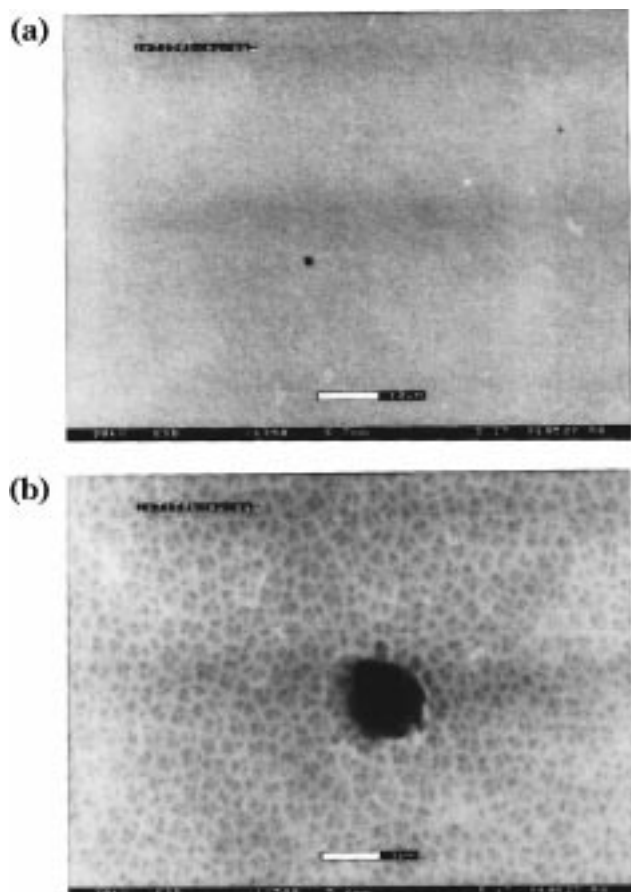
(25) Dayalan, E.; Peng, C. H.; Desu, S. B. *Ceram. Trans.* **1992**, *25*, 189.

(26) Barna, P. B. In *Diagnostics and Applications of Thin Films*; IOP Publishing Ltd.: London, 1992; p 295.

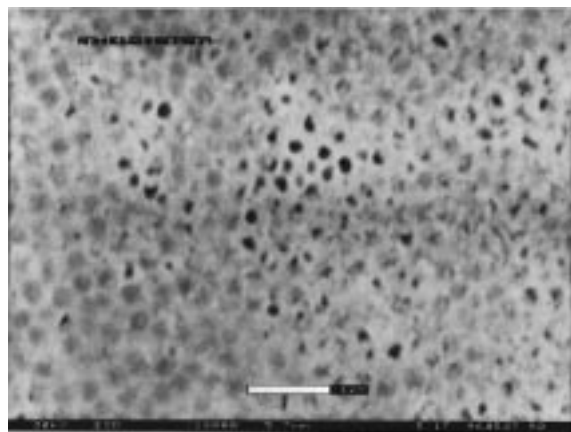
(27) Thompson, C. V.; Carel, R. *Mater. Sci. Eng.* **1995**, *B32*, 211.

(28) Venables, J. A.; Spiller, G. D. T.; Hanbucken, M. *Rep. Prog. Phys.* **1984**, *47*, 399.

(29) Srolovitz, D. J.; Goldiner, M. G. *JOM* **1995**, *43*, 31.



**Figure 4.** Typical example of additive experiments. The additive in this case was DEA: (a) scale bar, 10  $\mu\text{m}$ ; (b) close-up of hole in center of panel a; scale bar, 1  $\mu\text{m}$ . Note the texture visible which reflects the roughness of the underlying surface.



**Figure 5.** Example of a case where a continuous film did not form. The additive was ethylene glycol. Scale bar is 1  $\mu\text{m}$ .

stresses.<sup>30,31</sup> However, it may be instructive to examine our observations in light of the agglomeration seen in some films deposited by physical methods (electron beam evaporation, ion implantation, sputtering, PVD).

Film agglomeration, or dewetting, is associated with stresses in the film parallel to the substrate or with defects in the film providing nucleation points for holes.<sup>29</sup> Stresses are typically due to thermal expansion

mismatch and lattice mismatch. Since, however, the quartz substrates are amorphous, lattice mismatch should not be an issue. Likewise, thermal expansion mismatch between the quartz and the  $\text{BiCuVO}_x$  film is unlikely to be the cause of the agglomeration, since the  $\text{BiNbVO}_x$  films, which can be expected to have a thermal expansion coefficient (there is no measurement reported in the literature) similar to that of  $\text{BiCuVO}_x$ , did not show agglomeration on heating to the same temperatures. Another possible cause of the agglomeration seen in the  $\text{BiCuVO}_x$  films is the formation of intermediate molten or semiliquid phases during the annealing process. The agglomeration temperatures were well under the melting temperature of  $\text{BiCuVO}_x$  (895  $^\circ\text{C}$ ), and the  $\text{BiCuVO}_x$  phase is completely formed by 450  $^\circ\text{C}$ , well below the melting points of oxides that may be intermediates [ $\text{V}_2\text{O}_5$  (690  $^\circ\text{C}$ ),  $\text{Bi}_2\text{O}_3$  (825  $^\circ\text{C}$ ), and  $\text{BiVO}_4$  (880  $^\circ\text{C}$ )]. The stability of bulk  $\text{BiCuVO}_x$  indicates that low-melting phases would not have come about through decomposition of this phase; nor were other phases seen in the GIXRDs. Neither is there any indication that the  $\text{BiCuVO}_x$  reacted with the quartz substrate. Finally, the fact of the nonagglomeration of the  $\text{BiNbVO}_x$  films contradicts explanations of the  $\text{BiCuVO}_x$  agglomeration which involve the formation of other phases. These arguments suggest that the explanation for the agglomeration of the  $\text{BiCuVO}_x$  films at temperatures where  $\text{BiNbVO}_x$  films remained defect-free lies either in the energetics of the film-substrate interaction or in the precursor morphology.

The relative energies of adhesion of the film with itself (surface tension) and of the film with the substrate vary with the elemental composition of the ceramic film.<sup>26,28,29</sup> Therefore, one reason for the difference in the annealing behavior of the 30% Nb-doped and the 10% Cu-doped films lies in the relative strengths of the films' adhesion to the substrate versus their self-adhesion. This possibility is currently being explored. A second explanation may lie in the differences in precursor morphology due to the different methods of introducing the dopant. In the case of  $\text{BiNbVO}_x$ , the dopant is added as a hydrolyzable alkoxide which may be easily incorporated into the growing vanadium oxide polymer. Conversely, the  $\text{Cu}(\text{OAc})_2$  dopant may not be as homogeneously distributed in the precursor material, and copper atoms thus may be more likely to segregate to grain surfaces. Segregation of impurities—either the dopant metal or organics remaining from the precursor—onto grain surfaces may block grain growth and coalescence and contribute to the formation of grooves which subsequently deepen to expose bare substrate.<sup>26</sup> Also, the initial grain size, which depends on the metal oxide polymer cluster size and morphology, can contribute to the ease of void formation, as smaller grains lose matter to larger grains.<sup>29</sup> This material loss will be normal to the substrate and eventually will result in the formation of voids in the film.

*Additive Effects on Film Morphology.* On the hypothesis that the differences between the annealing behaviors of the  $\text{BiCuVO}_x$  and  $\text{BiNbVO}_x$  films were due to the precursor morphology (e.g., that the addition of the Nb dopant as a hydrolyzable material provided a critical level of precursor gel network connectivity absent in the  $\text{BiCuVO}_x$  (Cu added as  $\text{Cu}(\text{OAc})_2$ ) precursor), several

(30) Sekiguchi, T.; Sawano, M.; Eguchi, K.; Arai, H. *Solid State Ionics* **1990**, *40/41*, 502.

(31) Isenberg, A. O. *Solid State Ionics* **1981**, *3/4*, 431.

additives known for their sol-gel network modifying properties were tested for their effects on the film qualities. These materials were added in the quantity of 1 mole of additive per mole of alkoxide group, and were thus present in sufficiently small amounts that they were not expected to have affected the bulk solution viscosity. In most cases, BiCuVO<sub>x</sub> films from additive-containing precursors were worse than the additive-free control films (Figure 3a). Films produced from DEA-containing solutions were of superior density over much of the film, however, with some bare patches. (Figure 3b; compare to Figure 1b). On the other hand, BiNbVO<sub>x</sub> films were unaffected by the additives. Possibly the additives which gave the lowest quality films, namely, ethylene glycol, propanolamine, and triethanolamine, replace some or all of the 2MOE ligands on the vanadium center, producing a less-hydrolyzable complex. TEA and tripropanolamine (TPA) ligands are known to remain bound to vanadate (V) ions in aqueous solutions, as does DEA. However, work by Crans et al.<sup>32</sup> shows that TEA and TPA are bound by the central N and only two alcohol arms, leaving the third dangling. Drawing an analogy from TPA to the propanolamine (PA) used here, Crans' results suggest that the PA will be bound only on the amine end. Ethylene glycol also has the potential for a dangling alcohol group. Conversely, DEA is bound by the amine nitrogen and both alcohol arms, even in aqueous solution; this additive gave a fairly dense, albeit defective, film. These correlations suggest that the dangling alcohol group somehow limits coalescence either during the gelation stage or during grain growth.

A direct indication of the interaction level between the additives and the vanadium center in V-2MOE is found in the <sup>51</sup>V NMR data (Table 1). TEA and PD induce immediate precipitation of an insoluble complex when added directly to the V-2MOE solution. This behavior has been seen with other vanadium alkoxides,<sup>32-36</sup> and points to the reason for these addi-

tives' negative effects on the film quality. Multiple peaks appearing in the <sup>51</sup>V NMR of the DEA and EG samples indicate the presence of multiple vanadium-containing species, presumably with differing degrees of ligand substitution. The high upfield shifts of the V signal in these solutions indicates strong binding. The reasons for differences in film quality produced by precursor solutions with different additives are being investigated, as is the question of why the negative effects for films on quartz substrates seen in association with the use of the additives did not translate to films on the porous substrates.

### Conclusions

Defect-free BiNbVO<sub>x</sub> films were cast onto quartz substrates. Films of BiCuVO<sub>x</sub> on quartz substrates were initially homogeneous but showed agglomeration with increasing annealing temperatures. The higher number of hydrolyzable groups in the BiNbVO<sub>x</sub> precursor, leading to a more connected precursor network, is suspected to be the major reason for the superior film quality seen with this material. Network-modifying compounds added to the BiCuVO<sub>x</sub> precursor solutions did not significantly improve the quality of the resulting films, and in several cases had a deleterious effect on film quality due to interactions between the additive and the vanadium alkoxide. However, films of BiCuVO<sub>x</sub> were successfully cast onto porous alumina substrates.

The film agglomeration and concomitant void formation seen in the BiCuVO<sub>x</sub> films on quartz substrates exemplify the need for care in examining the behavior of a membrane device during thermal cycling.

**Acknowledgment.** This work was supported through NSF Grant DMR 9696235. J.W.P. wishes to acknowledge an NSF predoctoral fellowship.

CM960566F

(34) Nugent, W. A.; Harlow, R. L. *J. Am. Chem. Soc.* **1994**, *116*, 6142.

(35) Uchida, N.; Ishiyama, N.; Kato, Z.; Uematsu, K. *J. Mater. Sci.* **1994**, *29*, 5188.

(36) Mondal, S.; Rath, S. P.; Dutta, S.; Chakravorty, A. *J. Chem. Soc., Dalton Trans.* **1996**, 99.

(32) Crans, D. C.; Shin, P. K. *J. Am. Chem. Soc.* **1994**, *116*, 1305.

(33) Crans, D. C.; Felty, R. A.; Chen, H.; Eckert, H.; Das, N. *Inorg. Chem.* **1994**, *33*, 2427.