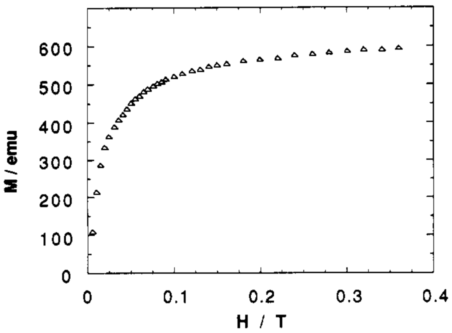

Figure 2. Magnetization (per mole of Fe) versus applied external magnetic field of intercalate 1, measured at 5 K.

Below 90 K, the magnetic susceptibility becomes very large, and field dependent but no longer temperature dependent. This suggests the onset in 1 of a magnetically ordered state associated with spontaneous magnetization. The following simple experiment is quite spectacular: when a Pyrex tube containing 1 is soaked in liquid nitrogen on top of a standard magnetic stirrer, the powder "flows" in the tube and follows the rotating rod; the phenomenon stops upon reheating.

Study of the magnetization *M* of material 1 as a function of the applied magnetic field has been carried out at 5 K using the Metronique Ingenierie SQUID magnetometer. Results are shown on Figure 2. The magnetization of the sample rapidly increases in low fields and then remains nearly constant in stronger fields. The saturation value of *M* (around 550 cgs emu/mol of iron) is only a fraction of the value expected (~22 000 cgs emu/mol of Fe) if all spins were ordered parallel. These results may be interpreted in terms of the onset of weak ferromagnetism in material 1. This phenomenon arises from the canting of antiferromagnetically coupled spins in such a way that a net moment results. Altenatively, the spontaneous magnetization may also arise from uncompensated moments around the metal vacancies (which introduce some frustration) in the antiferromagnetic Fe^{2+} lattice.

The electrical conductivity of 1 along the layers plane was measured on a monocristalline platelet between −50 and +50 °C by using a classical four-probe technique. The conductivity σ of 1 is very small ($\sigma = 6.6\ 10^{-7}\ \Omega^{-1}\ \text{cm}^{-1}$ at 25 °C) and thermally activated. A plot of log σ versus $1/T$ is linear and leads to an activation energy of $\approx$0.2 eV.

We note that syntheses carried out in the presence of a larger amount of pyridine result in a diphasic mixture consisting of material 1 and of a different $FePS_3$ intercalate characterized by a basal spacing of $\approx$12 Å. We also note that long exposure ($\approx$2 weeks) of material 1 to air results in partial hydrolysis of the P_2S_6 groups into phosphates (appearance of a broad IR band near 1100 cm^{-1}).

The reason intercalation of the lattice results in such spectacular modification of the magnetic properties is not definitively understood, because of the impossibility of obtaining a detailed X-ray structure of this type of material. We have shown in the past that intercalation of $MnPS_3$ causes local disorder and distortion around the metal, probably as a result of the creation of intralamellar vacancies that lower the local symmetry and introduce some frustration.[14] A better understanding of the role of intercalation is expected from EXAFS, Mossbauer, and neutron diffraction studies, which are currently in progress.

Acknowledgment. We thank E. Codjovi for his technical assistance.

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Preparation of Electrically Conducting Indium–Tin Oxide Thin Films by Heat Treatment of Mixed-Metal Hydroxide Dispersion Containing Polymer Binder

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ITO thin films are attractive materials for transparent electrodes and display panels, etc.,[1] and a variety of processes, such as vacuum evaporation,[2] radio frequency sputtering,[3] and spray pyrolysis[4] have been reported for the preparation of the ITO films. A more simple dip–dry–heat treatment method[5–7] has been also developed by using some organic compounds (e.g., alkoxide and acetylacetonate) of indium and tin. However, this method has not been applied to practical use since the pure organic compounds are relatively difficult to be prepared and expensive.

On the other hand, Woodhead and his co-worker reported that an indium hydroxide–tin hydroxide mixture highly dispersed in aqueous media (they called this dispersion system an aqueous sol/solution) gave a fine free-flowing ITO powder.[8] They also suggested usability of the aqueous sol/solution precursor as coating materials of metal wire and substrates. However, no report has been published on the usability of the aqueous sol/solution to prepare electrically conducting ITO thin film; this may be due to difficulty to prepare the electrically conducting ITO thin film because of aggregation of the metal hydroxide on substrate plates during the dip–dry process.

On the other hand, several kinds of water-soluble polymers, such as poly(vinyl alcohol) and (hydroxypropyl)cellulose, afford the indium hydroxide–tin hydroxide aqueous sol/solution with appropriate viscosity to prevent the aggregation of the metal hydroxide when added to the indium hydroxide–tin hydroxide aqueous sol/solution. The polymer binder can be easily removed by burning during firing of the indium hydroxide–tin hydroxide mixture. We now report preparation of the ITO thin films using the polymer-containing aqueous sol/solution.

Indium hydroxide–tin hydroxide mixture was first prepared by coprecipitation from an aqueous solution of $InCl_3$ and $SnCl_4$ (0–10% in Sn/(Sn + In) atomic ratio); a dilute aqueous ammonia was added to the aqueous solution of $InCl_3$ and $SnCl_4$. The resulting mixed hydroxide was washed with water repeatedly to remove NH_4Cl and collected by filtration.

The mixed hydroxide collected was then dispersed in water with vigorous stiring, and water-soluble polymer and dilute nitric acid were added to the hydroxide dispersion for preventing aggregation of the mixed hydroxide and controlling the pH of the dispersion systems (pH = 2–3),

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Table I. Characteristics of ITO Films Prepared from Indium Hydroxide–Tin Hydroxide Aqueous Sol/Solution Containing the Added Polymer[a]

	addition of polym		ITO thin film			
run	added polym (mw)	concn/wt %	film thickness/Å	$10^2\rho_s{}^b/\Omega$ cm	$10^3\rho_s{}^c/\Omega$ cm	opt transm[d]/%
1	poly(vinyl alcohol) (2.5×10^4)	4.0	900	2.8	3.7	95
2	poly(vinyl alcohol) (3.0×10^5)	1.5	800	2.0	1.8	97
3	(hydroxypropyl)cellulose (1.0×10^6)	0.075	700	1.6	1.3	97
4	poly(2-vinylpyrrolidone) (3.6×10^5)	3.0	800	2.1	2.8	88

[a] The precursor aqueous sol/solution contained 0.1 mol/L of indium hydroxide–tin hydroxide (Sn/(Sn + In) atomic ratio = 6 atm %), additive polymer, and dilute HNO_3. [b] Heating condition: 550 °C, 1 h under air. [c] Heating condition: 900 °C, 1 h under air, followed by annealing at 350 °C for 30 min under N_2 atmosphere. [d] At 550 nm.

respectively. As the water-soluble polymer, poly(vinyl alcohol), (hydroxypropyl)cellulose, and poly(2–vinylpyrrolidone) were used. Application of ultrasonic waves toward the disperse systems peptized well the polymer-containing aqueous sol/solution of indium hydroxide–tin hydroxide, and the resulting aqueous sol/solution was stable for 20 days at room temperature.

Sodalime glass or quartz glass substrate was coated with the polymer-containing aqueous sol/solution of indium hydroxide–tin hydroxide by pulling up the substrate dipped in the aqueous sol/solution at 58 cm min^{-1}. After drying at 70 °C for 10 min, the substrate coated with polymer–metal hydroxide thin film was fired in an electric furnace in the temperature range 350–900 °C for 1 h under air. Annealing of ITO thin film was carried out under N_2 atmosphere or vacuum (about 0.15 Torr) at 350 °C for 30 min. When necessitated, the dipping process and heat treatment were repeated to obtain a thicker ITO film.

The resulting thin films were characterized by X-ray diffractometry, UV–visible spectroscopy, and scanning electron microscopy. The thickness of the films was determined by multiple-beam interfering method. The electrical resistivity of the films was measured by using a Mitsubishi-Yuka MCP-T400 d.c. four-probe measuring unit.

Comparison of results of thermogravimetric analyses of poly(vinyl alcohol), the indium hydroxide–tin hydroxide mixture, and dried poly(vinyl alcohol)-containing indium hydroxide–tin hydroxide mixture revealed that decomposition of the added poly(vinyl alcohol) started at 200–220 °C, whereas thermal desiccation of the sol occurred in the wide temperature range 100–350 °C.

The obtained films were smooth and fine-grained with thickness of 800–900 Å and exhibited 95–99% of transmission in the visible range (400–760 nm). X-ray diffraction patterns showed peaks of polycrystalline In_2O_3. By using hydroxypropyl cellulose and poly(2-vinylpyrrolidone), similar ITO thin films were obtained.

The electrical resistivity of the films showed a minimum value at 6 atm % of Sn (SnO_2) content. Figure 1 shows dependence of the specific resistivity (ρ_s) on heating temperature for the In_2O_3 film containing 6 atm % of Sn. The electrical resistivity of the films decreased with increase in the firing temperature. X-ray diffraction patterns suggested that electrical resistivity of the ITO film decreased with increase in the crystallinity of In_2O_3 by raising the firing temperature. The specific resistivity was comparable or somewhat higher compared with those (1.3×10^{-3}–8×10^{-3} Ω cm) of reported ITO films prepared by thermal decomposition of organometallic compounds.[5-7]

It is reported that annealing of ITO film under N_2 or H_2 atmosphere or in vacuum affects the electrical resistivity of the ITO films.[5,9] As depicted in Figure 1, annealing of the present ITO film also led to a decrease in the ρ_s values of 0.5 or 1 order of magnitude. It is inferred that the annealing increases the carrier concentration by increasing the number of oxygen vacancies and improves homogeneity of the ITO film presumably due to further solid reaction of In_2O_3 and SnO_2.[5,9] The lowest specific resistivity of 1.3×10^{-3} Ω cm was thus achieved by the firing at 900 °C and ensuing annealing at 350 °C under N_2. A repeated coating–heating process gave a smooth ITO film with thickness of 2400–2500 Å, and this film showed sheet resistivity of 75 Ω cm^{-2}. The ITO film thus obtained showed 87% of transmittance at 550 nm.

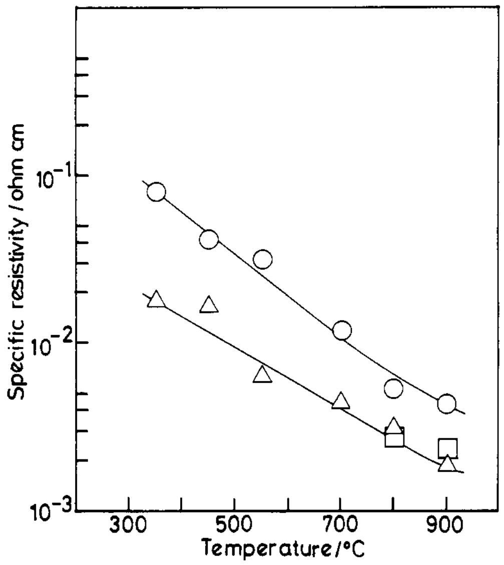

Figure 1. Dependence of specific resistivity of ITO thin films containing 6 atm % of Sn (SnO_2) on firing temperature; ○, the ITO film prepared by firing at the temperature; △, the ITO film prepared by the firing at the shown temperature (Abscissa) and ensuing annealing at 350 °C under N_2 atmosphere; □, the ITO film prepared by the firing at the shown temperature and ensuring annealing at 350 °C under vacuum (0.15 Torr). The precursor aqueous sol/solution (pH 3.0) contained 0.1 mol/L of the metal hydroxide and 1.5 wt % of poly(vinyl alcohol).

As described above, addition of the water-soluble polymer afforded the transparent and conducting ITO films; however, the aqueous sol/solution without the polymer gave a heterogeneous and turbid film due to the aggregation of the metal hydroxides on the glass substrate.

Table I summarizes the electrical and optical properties of the ITO films obtained from the aqueous sol/solution containing the polymer. Poly(vinyl alcohol), (hydroxypropyl)cellulose, and poly(2-vinylpyrrolidone) formed the stable aqueous sol/solution and gave the transparent ITO film with high electrical conductivity. It suggests that these polymers have appropriate interaction to prevent aggregation of the metal hydroxides during dipping and drying processes. On the contrary, other water-soluble polymers including poly(acrylic acid), poly(methacrylic acid), and poly(acrylamide) did not give the highly dispersed aqueous sol/solution because of the precipitation

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of indium hydroxide and tin hydroxide in the presence of these polymers; this seems to be due to too strong interaction of these polymer with the metal hydroxides. Poly(acrylamide) is known to serve as coagulant of colloidal materials.[10]

The smoothness and transparency of the ITO film depended on the amount of added polymer, and the best results were obtaied at the concentration shown in the third column of Table I. Addition of larger amounts of the polymer caused an increase in the amont of volatile component during the heat treatment and hindered formation of the homogeneous ITO thin film. As shown in Table I, addition of less amount of poly(vinyl alcohol) was enough when the molecular weight of the polymer increased.

The present ITO film on the glass substrate can be prepared with good reproducibility. Due to the simplicity of the process to form the ITO film from simple compounds, the present process will serve as useful method for the preparation of the electrically conducting ITO thin films with large area.

Registry No. ITO, 50926-11-9; indium hydroxide, 20661-21-6; tin hydroxide, 12054-72-7; poly(vinyl alcohol), 9002-89-5; poly(2-vinylpyrrolidone), 9003-39-8; hydroxypropylcellulose, 9004-64-2.

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(10) Japan Analytical Chemistry Association, *Handbook of Polymer Analysis*; Asakura Syoten, 1962; p 443.

Crystal Structure of a New Lead Zinc Acetate Alkoxide, $Pb_2Zn_2(C_2H_3O_2)_4(C_3H_7O_2)_4$

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Sol–gel processing is a popular and versatile method for the preparation of glasses and ceramics in monolithic shapes, fine powders, fibers, and thin layers.[1] The first step in polymeric sol–gel processing is the synthesis of a solution containing the requisite metal cations. Commonly, the solution is comprised of metal alkoxides ($M(OR)_x$) in an alcohol solvent. Addition of water to an alkoxide solution results in hydrolysis followed by condensation reactions, network formation, and the eventual development of a continuous polymeric gel. The heterometallic alkoxides can be viewed as molecular precursors or "building blocks" for the development of gel networks and the synthesis of ceramic materials. While many alkoxides have been synthesized and used successfully in sol–gel processing, some metal alkoxides have low solubility, are difficult to prepare, and are not stable with time.[2] Consequently, the exclusive use of alkoxides for multicomponent sol–gel solutions is sometimes not possible, and often alternative precursors are necessary, especially for specific components.

Metal acetates are often used in combination with alkoxides in sol–gel systems due to their solubility, convenience, and thermolysis behavior. The formation of heterometallic species by the reaction of acetates with alkoxides has been reported,[3-5] and as will be described in the present research, metal acetates can react in alcohol to form a different type of precursor, a heterometallic acetate alkoxide. The structure and composition of precursors formed in solution should be characterized so as to obtain a better understanding of the hydrolysis and gelation reactions and for the control of final properties in the gel and the resulting ceramic. To this end, structural investigations of precursors isolated in single-crystal form provide valuable information.

In this report, the preparation and crystal structure of a heterometallic acetate alkoxide, $Pb_2Zn_2(C_2H_3O_2)_4(C_3H_7O_2)_4$, are described. Single crystals were isolated from a lead zinc acetate based precursor solution used for the sol–gel processing of lead zinc niobate, $Pb(Zn_{1/3}Nb_{2/3})O_3$ (PZN),[6] a useful electrical ceramic. The sol–gel process is of interest for the fabrication of improved ceramic devices from chemically derived powders and for the spin-casting of thin layers from sol–gel precursor solutions. To prepare a multicomponent PZN solution, however, alternative precursors are necessary. Because lead and zinc alkoxides are difficult to synthesize and not commercially available, a lead zinc acetate based precursor has been developed. Used in combination with niobium alkoxide, the new precursor allows for the synthesis of a PZN solution and the subsequent preparation of ceramic powders and thin layers by sol–gel processing.[6]

To prepare a Pb, Zn precursor solution, $Pb(C_2H_3O_2)_2\cdot 3H_2O$ and $Zn(C_2H_3O_2)_2\cdot 2H_2O$ were combined in a 3:1 molar ratio, dissolved in 2-methoxyethanol (HPLC grade, 8 mol of alcohol/mol of Pb), and heated. Volatiles were removed by distillation until the temperature of condensing vapors reached 124 °C, the boiling point of 2-methoxyethanol. The solution was then diluted with 2-methoxyethanol, and the distillation repeated twice. The distillation procedure was necessary to remove water from the Pb, Zn precursor solution, which was subsequently combined with a water-sensitive niobium alkoxide. During the final distillation, the Pb, Zn precursor solution was concentrated to approximately 3 M, based on Pb content.[7] Small cube-shaped crystals formed at room temperature within 24 h. After 96 h, the crystals grew to between 1 and 10 mm. Chemical analysis indicated the formation of $Pb_2Zn_2(C_2H_3O_2)_4(C_3H_7O_2)_4$ (anal. found Pb, 0.406, Zn, 0.127, C, 0.214, H, 0.0361; calcd Pb, 0.383, Zn, 0.121, C, 0.222, H, 0.0370). The $Pb_2Zn_2(C_2H_3O_2)_4(C_3H_7O_2)_4$ crystals could be redissolved in 2-methoxyethanol[8] and were air and water sensitive.

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(7) For preparation of PZN alkoxide based solution, the concentration of the Pb, Zn precursor solution is ~1 M, and crystals do not form.

(8) The crystals were soluble in 2-methoxyethanol, but a precipatate eventually formed in solutions with higher concentrations (>0.5 M).

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