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Structural and Electrical Properties of Sol–Gel-processed $CdTiO_3$ Powders and Films

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Cadmium titanate, $CdTiO_3$, was prepared by the sol–gel technique in bulk and in thin film form. The thermal evolution of the gels and the phase changes were studied by thermogravimetric analysis (TGA), X-ray diffractometry (XRD) and Raman and energy-dispersive (EDS) spectroscopies. The morphology of the samples was observed using scanning electron microscopy (SEM). Gels heated to 800 °C gave rise to powders with only the ilmenite-like phase. The orthorhombic perovskite phase is the only crystalline phase observed after a 4 h heat-treatment at 1100 °C. With respect to the conventional preparation method by solid-state reaction, by the sol–gel method it is possible to prepare the ilmenite phase at lower temperatures and the perovskite phase in a shorter time. Clear, homogeneous thin films were obtained by the dip-coating method. The refraction index and the thickness of the films were measured using ellipsometry. The humidity-sensitive electrical properties were measured for thin films deposited on alumina substrates with comb-type gold electrodes, heated to 200 °C and 450 °C. The films heated to 200 °C, which still contained organics, showed a variation of the resistance of six orders of magnitude in the relative humidity (RH) range tested (4–87% RH). The films heated to 450 °C, made of ilmenite-type $CdTiO_3$, were nearly insensitive to RH. © 1997 by John Wiley & Sons, Ltd.

Keywords: $CdTiO_3$; sol–gel; thin films; powders; Raman spectroscopy; X-ray diffraction (XRD); scanning electron microscopy (SEM); electrical properties; structural properties; humidity sensors

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INTRODUCTION

The titanium-based oxides with perovskite structure are widely used for electro-optic applications, mainly because of their ferroelectric properties.[1] They have been actively studied on account of their dielectric, piezoelectric, pyroelectric and photostrictive properties, which make these ceramics eligible to be defined as 'smart'.[2] The titanium-based oxides also showed interesting properties as humidity sensors.[3–5]

The conventional preparation method for these mixed oxides is the solid-state reaction at high temperatures of the corresponding single oxides. It is difficult, however, to obtain the pure mixed phase with the ceramic method, since residual amounts of the starting oxides are likely to remain in the final product unless repeated cycles of milling and heating are performed. The powders obtained are coarse, with rather a wide size distribution and a low specific surface area, given that the synthesis occurs at high temperatures.

Among the titanium-based oxides with the perovskite structure, cadmium titanate ($CdTiO_3$) is much less studied because it is not ferroelectric at room temperature. From a fundamental point of view, however, $CdTiO_3$ represents an interesting system for the investigation of the nature of the ferroelectric and structural phase transitions. In addition, like other titanium-based systems, there is the possibility that it may have unexplored potential for application in non-linear optics.

$CdTiO_3$ crystallizes into a hexagonal ilmenite ($FeTiO_3$)-like structure below 1000 °C, and into an orthorhombic distorted perovskite structure when it is sintered above 1050 °C. Its ferroelectric properties at low temperature (< 50 K) are not well understood and are subject to controversy.[6–8]

$CdTiO_3$ is usually prepared by heating CdO

and TiO_2 at temperatures around 1000 °C (ilmenite phase) or over 1200 °C (perovskite phase). The duration of the treatment varies between 24 and 36 h at ordinary pressure, being reduced to 60 min at 1.5 GPa.[9] Thus, another reason which might have limited the number of studies on $CdTiO_3$ is the use of toxic CdO in its conventional preparation method.

Much effort has recently been dedicated to the development of innovative chemical methods in order to lower the preparation temperature and to obtain ultrafine and chemically pure powders of mixed oxides.[10] For the preparation of perovskite-type oxides, methods have been developed which include sol–gel and hydrothermal treatments, pyrolysis or thermal decomposition of precursors precipitated by wet-chemical procedures.[11]

Another important issue to be considered is the recent significant interest in ferroelectric thin films[12] for new potential applications unique to thin films,[13] which include non-volatile memory devices[14] and applications in integrated optics.[15] The use of thin films is also one of the most important recent requirements of materials for integrated chemical sensors.[16,17] Thin films of titanium-based oxides with perovskite structure can be prepared by physical methods such as sputtering,[18,19] or chemical methods, such as sol–gel techniques.[20,21] The sol–gel preparation method permits the direct preparation of high-purity ceramics in their final film shape.[22] The use of thin films prepared by the sol–gel method has been shown to be particularly promising for humidity sensors.[23] Sol–gel-processed lead titanate and zirconate thin films have been studied by some of the authors of this paper for application in multifunctional humidity sensors.[24]

In this paper, the preparation and the characterization of cadmium titanate in bulk and in thin film form by a sol–gel method are reported. A room-temperature procedure has been attempted experimentally in this work, there being a lack of papers in the literature about the sol–gel synthesis of these materials. Preliminary results of the humidity-sensitive electrical properties of the films are reported.

EXPERIMENTAL

Materials

The following reagents were used for the synthesis: $Cd(CH_3COO)_2 \cdot 2H_2O$ (Carlo Erba), $Ti(O^iPr)_4$ (Fluka; ^iPr = isopropyl), $CH_3OCH_2CH_2OH$ (Aldrich), HNO_3 (Carlo Erba, RPE). The composition was such as to have a molar ratio Ti : Cd = 1:1. The concentration, expressed in oxides, was 100 g l^{-1}. Nitric acid was added to the solution of cadmium acetate in alcohol to obtain a pH value equal to 2, in order to avoid the formation of precipitates. Then $Ti(CH_3OCH_2CH_2O)_4$ was added, obtained by distillation of $Ti(O^iPr)_4$ in methoxyethanol under a nitrogen atmosphere. The final solution was stirred for several hours.

The solution, after reaching a high viscosity, was heated to 40 °C in a furnace to enhance the evaporation rate and speed up the gel formation. The gel obtained was heated to 120 °C and gave rise to a bright yellow powder. At room temperature, the product appeared to be rubbery and with a high tendency to absorb water during cooling, because of its high hygroscopicity. A further treatment at 180 °C produced a less hygroscopic material.

Bulk samples of the gel were heat-treated under an air atmosphere from 300 to 1100 °C, using a heating rate of 120 °C h^{-1}, with a dwell time of 30 min every 100 °C. At the beginning of every new temperature ramp, portions of powder were withdrawn from the furnace and subjected to the various analyses.

Mono- and multi-layer films were prepared on microscope (glass) or on quartz slides by a dip-coating method, using different withdrawal speeds. The solution used for depositing films with the dipping method had the same composition as that used for gel preparation, but it was more dilute. In fact, problems with film homogeneity were observed at high concentrations.

The as-deposited films were first dried at 120 °C; after cooling they were white and opaque. A further treatment at 450 °C for 30 min made the films transparent. Besides glass, aluminium and steel were also used as the substrates: adherence and homogeneity were very good, which made these samples very interesting. For electrical measurements, prototype sensors were prepared by depositing the films on Al_2O_3 substrates with comb-type gold electrodes. The films were deposited using a withdrawal speed of 14 cm min^{-1}. The films obtained, after drying, were heat-treated to 200 °C and 450 °C for 24 h.

Multilayer samples were prepared by making subsequent deposits on the same substrate, and treating every film obtained for 30 min at

450 °C. A series of 19 thin layers was successfully obtained, with good homogeneity. These films underwent different thermal treatments in the temperature range 400–1100 °C.

Measurements

The thermal evolution of the gel was studied by thermogravimetric analysis (TGA, Perkin-Elmer model TGA7), with a heating rate of 10 °C min^{-1} in flowing air. Crystalline phases of powdered bulk gels were identified by using a powder X-ray diffractometer (Phillips PW1050), with Cu Kα radiation ($\lambda = 1.54178$ Å). Raman spectra were collected with back-scattering geometry with a double monochromator (SPEX 1403), and a Coherent 2020 Ar^+ laser ($\lambda = 5145$ Å) as the light source. Energy-dispersive spectroscopy (EDS; model Link eXL II) was used to characterize powders and films. The morphology of powders and films was observed by scanning electron microscopy (SEM), using a Leica Cambridge Stereoscan 360. The thickness and refraction index of the films were determined with a precision ellipsometer EL X-1 (DRE–Dr. Riss Ellipsometerbau GmbH), using a He–Ne laser source ($\lambda = 632.8$ nm).

The humidity-sensitive electrical response of the specimens was evaluated by electrochemical impedance spectroscopy (EIS) measurements, using a frequency response analyzer (Solartron 1255) equipped with a home-made high-impedance adaptor. EIS spectra were recorded in the frequency range 10^{-2}–10^5 Hz at 40 °C and relative humidity (RH) values ranging from 4 to 85%, obtained by mixing dry and water-saturated air. The resistance values were evaluated on the complex impedance plane plot, from the intercepts of the semiarcs at high frequencies of the EIS spectra with the real axis. The monitoring of RH within the test chamber was carried out using a hygrometric probe (Ultrakust model F3000), which gave results accurate to within ±2%.

RESULTS AND DISCUSSION

$CdTiO_3$ powders

Figure 1 shows the TGA curve in air of the sol. The weight loss started slowly at about 50 °C and the first step was completed at about 160 °C. The weight loss in this temperature range was 11.4%. Since the sol is hygroscopic, this loss can

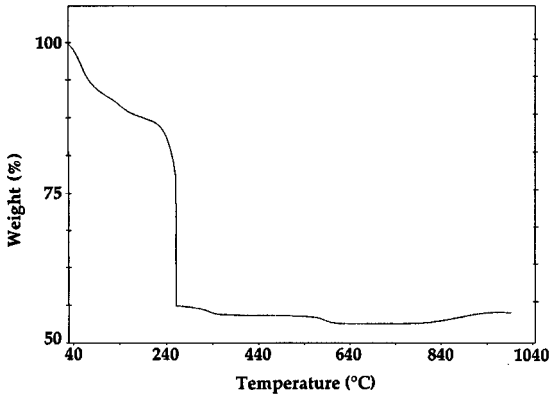

Figure 1 TGA curve of the sol, measured in flowing air at a heating rate of 10 °C min^{-1}.

be ascribed to the release of adsorbed water and to the evolution of acetic acid remaining in the sol, derived from the starting acetate. A further weight loss of 32.5% was observed up to 280 °C. This loss was rather fast; this was attributed to the combustion of residual organics.

The results of the XRD analysis of the powders heated at various temperatures are shown in Fig. 2. The only crystalline phase present in the powders heated to 300 °C and 400 °C was CdO, while at 500 °C peaks of $CdTiO_3$ in its hexagonal form started to appear. As the temperature of the powder treatment was increased, the intensity of the CdO peaks decreased and CdO was not present in the sample heated to 800 °C. The opposite behavior was noticed for $CdTiO_3$, in its hexagonal form, with an increase in the peak intensities up to heating at 900 °C. Traces of TiO_2, in the anatase structure at 600 °C and in the rutile structure at temperatures $\geqslant 700$ °C, were also observed. This can be explained by the volatilization at high temperatures of a small fraction of cadmium.

The presence of a new phase, identified as orthorhombic $CdTiO_3$, was clearly evident for the samples heated to 1100 °C for 4 h. Figure 3 shows a comparison between the experimental and the calculated XRD patterns for orthorhombic cadmium titanate. However, the amount of rutile was ever-increasing with the heating temperature. Moreover, samples treated at 1100 °C for 1 day showed the presence of a larger amount of rutile with respect to the sample treated at the same temperature for 4 h. This would confirm cadmium volatilization.

In order to confirm that the formation of TiO_2 was due to the lack of cadmium due to

volatilization, a different sample containing an excess of cadmium (molar ratio Cd : Ti = 1.3:1.0) was synthesized and underwent similar treatments. Figure 3 also shows the XRD profile of the excess-cadmium sample heated to 1100 °C for 4 h. One may observe that the phases detected were CdO and orthorhombic $CdTiO_3$, as expected in agreement with the hypothesis put forward.

Figure 4 shows the EDS spectra obtained for the $CdTiO_3$ powders heated to 500 °C and 1100 °C for 4 h. The same experimental conditions were used to measure both samples. EDS patterns showed the sole presence of the cadmium and titanium peaks for both powders. One can clearly observe that, even without quantitative analysis, the intensity ratio of cadmium/titanium peaks varied, being poorer in cadmium for the powder heated to 1100 °C. This is a further confirmation of cadmium volatilization at high temperatures.

The morphology of the powders was observed by SEM. Figure 5 shows the SEM micrographs at different magnifications of the powder sample heated to 500 °C for 4 h. As shown in Fig. 5(a), this powder consisted of large particles (average size 2 μm), probably agglomerated during drying due to the occurrence of capillary forces (Fig. 5b). The presence of sub-units of the micronic grains was not detected by SEM. The presence of large pores is also evident, which can be due to the thermal evolution of the residual organics from the gel. The powder heated to 1100 °C was made of very large, spongy aggregates (Fig. 6a), easily destructible by a limited mechanical pressure, which enables the collapse of the large pores. The presence of the large craters could be attributable to the cadmium volatilization. These aggregates are made of agglomerates of a few micrometers, which in turn consist of particles ranging between 60 and 200 nm (Fig. 6b).

Raman spectra recorded on the same powders treated at different temperatures and subjected to XRD measurements are shown in Fig. 7. A small

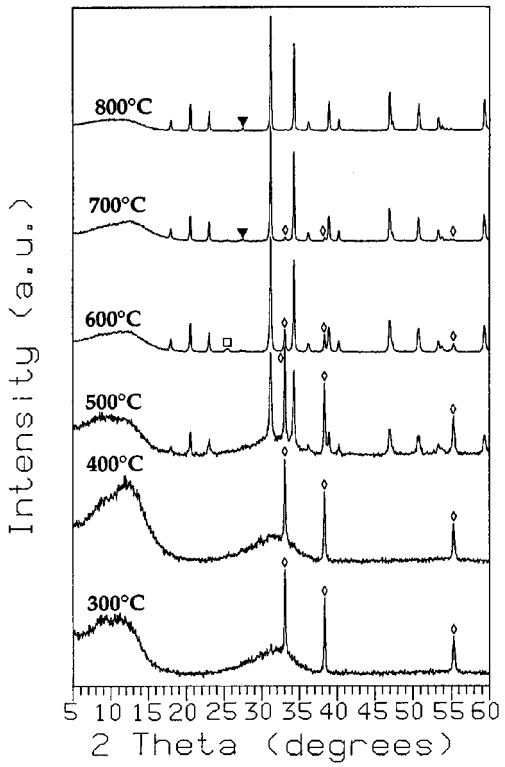

Figure 2 XRD profiles recorded on powders heat-treated for 30 min to various temperatures (◇, CdO; □, TiO_2 anatase; ▼, TiO_2 rutile; unmarked peaks correspond to $CdTiO_3$ in the hexagonal phase).

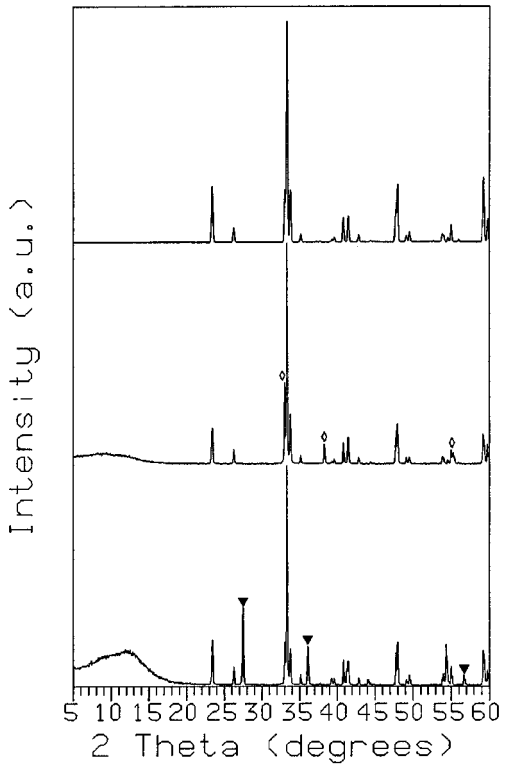

Figure 3 XRD profiles of the stoichiometric sample heated to 1100 °C for 4 h (bottom) and of the sample with excess cadmium heated to the same temperature (middle); the calculated pattern of the $CdTiO_3$ perovskite phase is also shown. ▼, TiO_2 rutile; ◇, CdO; unmarked peaks correspond to $CdTiO_3$ in the perovskite-type phase.

amount of TiO_2 (anatase), hardly detectable in XRD analyses, was revealed, and it had already disappeared at 800 °C. Furthermore, the spectra confirmed the presence of ilmenite-like $CdTiO_3$, whose pattern reproduces the pattern reported in the literature.[25]

The determination of the perovskite phase was much more difficult. Figure 8 shows the Raman spectrum of the sample heated to 1100 °C for 24 h. Rutile gives a very strong Raman signal, even if present in small amounts, so that the peaks of titanium oxide hide weaker signals due to other compounds. In order to avoid the presence of TiO_2, the Raman spectra were performed on a cadmium-rich sample (Cd : Ti = 1.3:1.0), heated to different temperatures. In fact, the Raman spectra of powder obtained from this sample by heating between 800 °C and 1100 °C showed no TiO_2 phases, but the presence of a large amount of CdO. CdO has a very weak Raman spectrum of its own, which caused the weakening of the whole Raman signal due to its large light absorption. As an example, the Raman spectrum of the sample heated at 800 °C, which contains the hexagonal phase of $CdTiO_3$ according to the XRD results, is reported

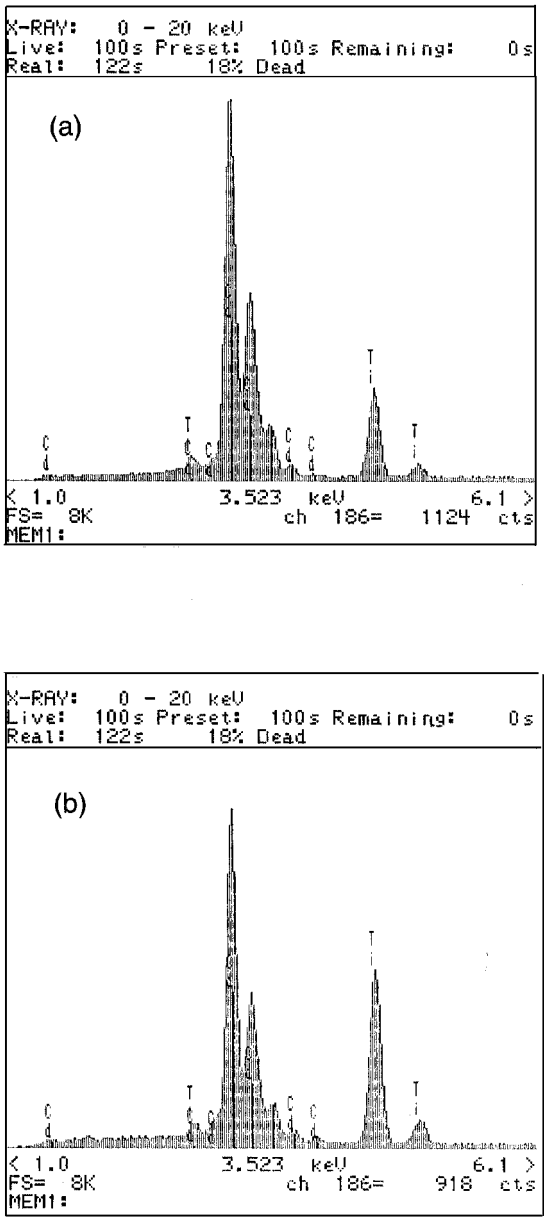

Figure 4 EDS spectra of powder samples of $CdTiO_3$ heated to (a) 500 °C and (b) 1100 °C.

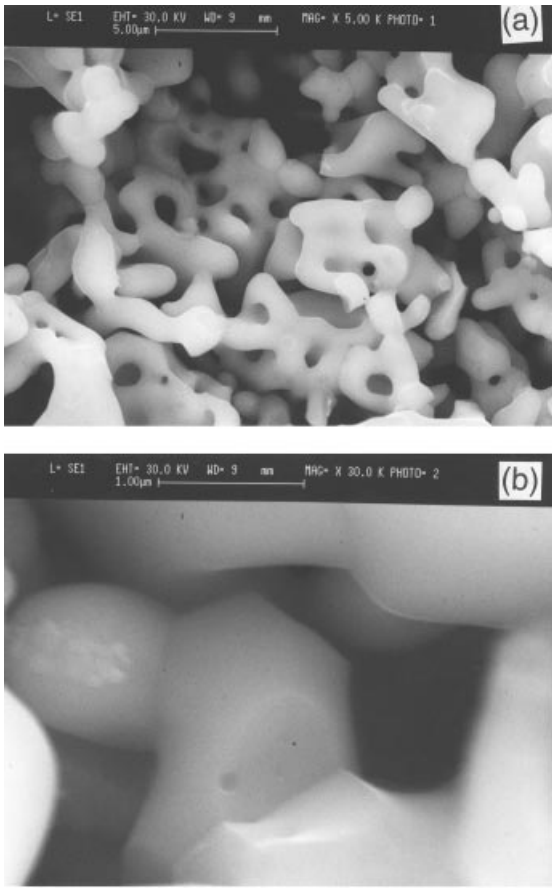

Figure 5 Scanning electron micrographs of powder samples heated to 500 °C, at (a) low and (b) high magnifications.

in Fig. 9. The Raman spectrum of ilmenite-like $CdTiO_3$ was not detectable.

It was decided to prepare a new sample with a minor excess of cadmium (Cd : Ti = 1.05:1.00), in order to try to reduce the absorption effects. The powders obtained were treated directly at 1100 °C. Figure 10 shows the resulting Raman spectrum of the perovskitic phase obtained. This

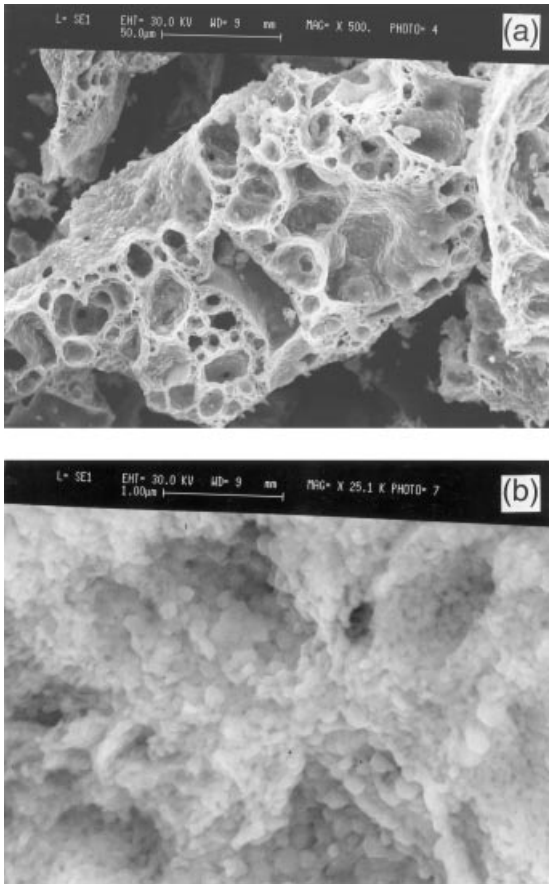

Figure 6 Scanning electron micrographs of powder samples heated to 1100 °C, at (a) low and (b) high magnifications.

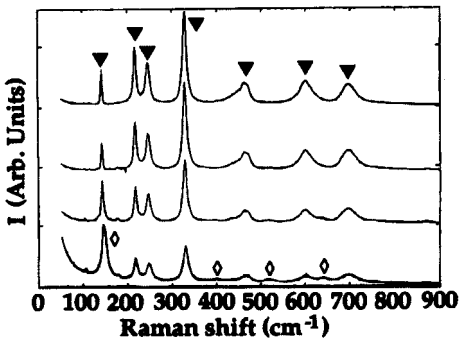

Figure 7 Raman spectra of the powder samples heated to 600 °C, 700 °C, 800 °C and 900 °C, from bottom to top (▼, hexagonal $CdTiO_3$; ◇, TiO_2 anatase).

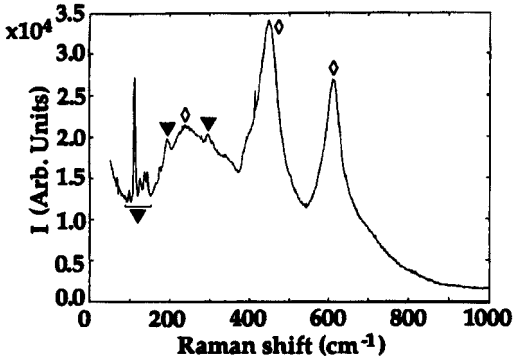

Figure 8 Raman spectrum of the powder sample heated to 1100 °C (▼, perovskite-type $CdTiO_3$; ◇, TiO_2 rutile).

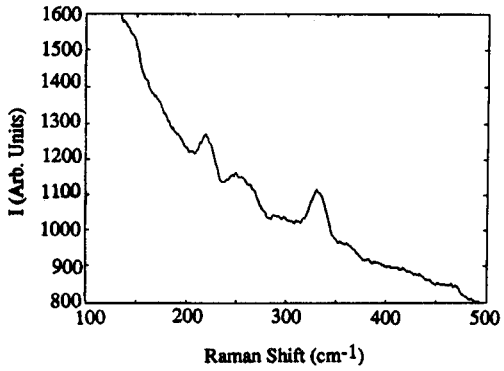

Figure 9 Raman spectrum of the sample with a Cd/Ti molar ratio of 1.3:1.0 heated to 800 °C.

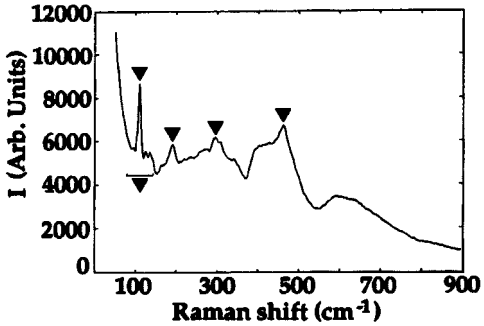

Figure 10 Raman spectrum of the sample with a Cd/Ti molar ratio of 1.05:1.0, heated to 1100 °C (▼, perovskite-type $CdTiO_3$).

Raman spectrum shows the features of orthorhombic $CdTiO_3$. To the authors' knowledge, this is the first published Raman spectrum for perovskite-type $CdTiO_3$.

Structural analysis of $CdTiO_3$ films

In order to carry out XRD analysis, multilayer samples were prepared with the aim to increase their thickness. Initially, the layers were amorphous. A treatment at 450 °C for 48 h made the film opalescent. XRD measurements confirmed the presence of rhombohedrical $CdTiO_3$, as shown in Fig. 11(a), also in the films. Quartz slides were used as substrates to perform heat-treatments at higher temperatures. The multilayer sample was heated to 1100 °C for 24 h. Unfortunately, as shown in Fig. 11(b), the XRD pattern showed the presence of TiO_2 (rutile), together with traces of perovskite-type $CdTiO_3$. To obtain the perovskitic phase a prolonged heat treatment at high temperature is necessary, but cadmium evaporation does not permit the formation of pure $CdTiO_3$ starting from a stoichiometric sol.

These results prompted us to study the humidity-sensitive electrical properties of the films heated at low temperatures, in order to obtain an amorphous film (at 200 °C) and an ilmenite-type $CdTiO_3$ film (at 450 °C). This choice is also consistent with the previous findings of some of the authors of this paper, which showed that a large humidity response was obtained for sol–gel-processed films (TiO_2-based and iron oxide-based) heated to temperatures lower than 500 °C.[26]

Figure 12 shows the SEM micrographs of the surface of the films prepared for the electrical measurements, heated to 200 °C (Fig. 12a) and to 450 °C (Fig. 12b). The films heated to 200 °C consisted of a thin layer covering the grains of the alumina substrate, without any pores. The film heated to 450 °C was still dense, but the formation of nano-sized grains coud be detected.

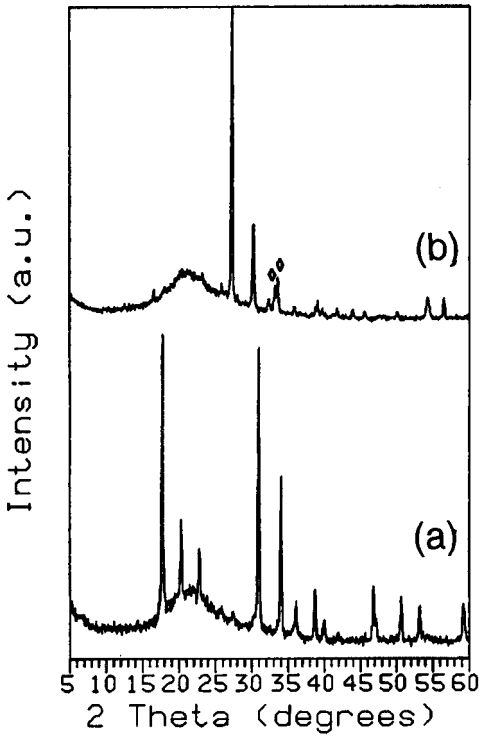

Figure 11 XRD profiles of multilayer films treated at (a) 450 °C (hexagonal $CdTiO_3$) and (b) 1100 °C (◇, perovskite $CdTiO_3$; unmarked peaks correspond to rutile TiO_2).

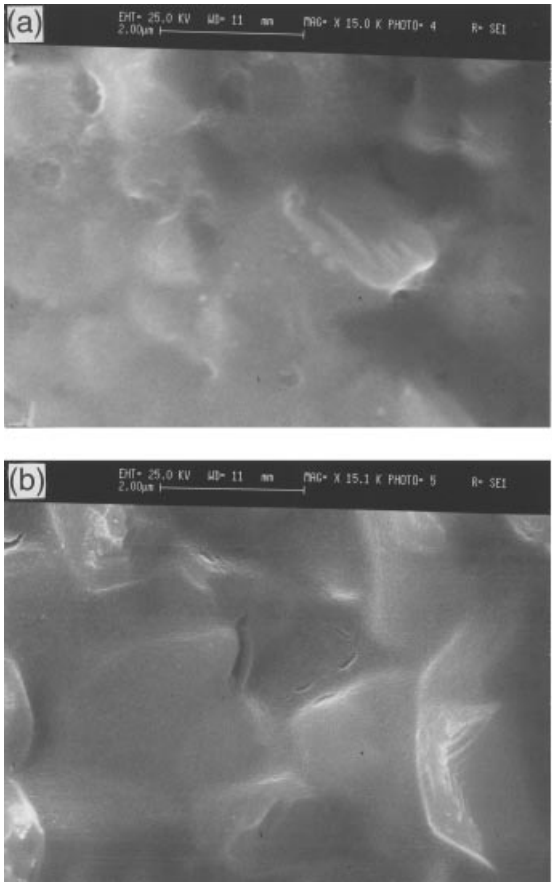

Figure 12 Scanning electron micrographs of the surface of thin films heated to (a) 200 °C and (b) 450 °C.

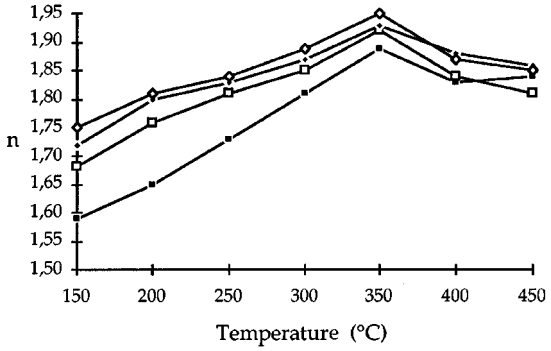

Figure 13 Refractive index (n) of the films (at $\lambda = 632.8$ nm) as a function of treatment temperature and of withdrawal speed (■, 4.4 cm min^{-1} □, 14 cm min^{-1}; ◆, 22 cm min^{-1}; ◇, 26.8 cm min^{-}1).

In this case also, as for the powders, EDS measurements showed a decrease in the Cd/Ti ratio of their peak intensities with an increase in the heating temperature, although the decrease was less strong.

Figure 13 shows the results of the ellipsometric measurements, which permitted evaluation of the changes of the refractive index (n) as a function of the treatment temperature and of the withdrawal speed from the solution, a parameter which affects the film thickness. The refractive index increased with increasing withdrawal speed, and consequently with increasing thickness. The refractive index also increased with increasing film heating temperature up to 350 °C. At this temperature the hypothesis of CdO formation can be assumed, which would cause a change in the slope. Data relating to samples treated at 450 °C again show an increase in n, due to the formation of ilmenite-like $CdTiO_3$. It must be taken into consideration that in this region the differences among the measurements are close to the experimental errors (from 0.01 to 0.03), so that the final resulting values of n are all constant and equal to each other.

It is also possible to obtain the values of the thickness by ellipsometry. Due to the irregular surface of the substrate, the films exhibited thickness variations from point to point. All the measured values fell in the range 105–170 nm. The trend of the thickness variation with the treatment temperature was similar to that of the refractive index variation (as thickness decreases, material density and refractive index increase). The phase transformation probably affects both the thickness and the refractive index of the film.

Humidity-sensitive electrical properties of $CdTiO_3$ films

The complex impedance plots recorded at 4% RH and 40 °C for the films heated to 200 °C and 450 °C showed the presence of a single semicircle, slightly inclined to the real axis. The spectrum loci decreased with increasing RH for both films, but the evolution was completely different. For the film heated to 450 °C, the plots were slightly affected by RH. At all the RH values tested, a single semicircle was observed. For the film heated to 200 °C, a single semiarc was observed for RH $\leqslant 30\%$, while at higher RH values the spectrum loci decomposed into a semicircle at high frequencies and a linear spur at low frequencies, which is a Warburg-like line. A dramatic decrease in resistance with increasing RH was observed, besides a progressive increase in the frequency at the maximum of the semicircles in the complex impedance plane plots. As an example, Fig. 14 shows the impedance data measured at 50% RH for the films heated to 450 °C, presented in the complex impedance plane plot (Fig. 14a) and in the Z'' and M''

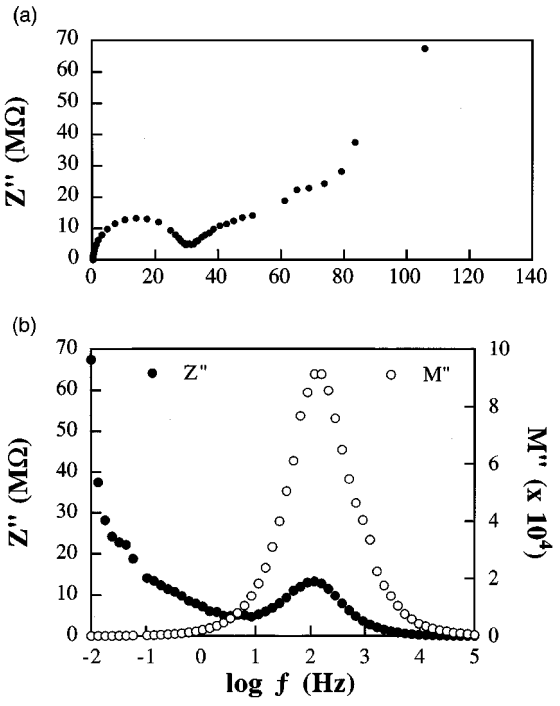

Figure 14 Impedance data for thin films heated to 200 °C, measured at 50% RH and 40 °C, presented (a) in the complex impedance plane plot and (b) in the Z'' and M'' spectroscopic plots.

spectroscopic plots (Fig. 14b), where Z'' is the imaginary part of the complex impedance and M'' is the imaginary component of the complex electric modulus.[27] The M'' spectroscopic plot showed only the peak at high frequencies, demonstrating that the capacitance values at low frequencies were very high.

Figure 15 shows the RH dependence of the resistance of the films heated to 200 °C and 450 °C, evaluated from the EIS spectra. The films heated to 450 °C were almost insensitive to RH, while the response of the films heated to 200 °C spanned six orders of magnitude over the whole RH range tested. The large RH response of these films cannot be explained in terms of the ionic-type sensing mechanism,[17] due to the fact that the films are free of capillary pores. Such a high humidity sensitivity has been reported for sol–gel-processed dense films, based on alkali-doped titania and on magnetite.[26] For alkali-doped titania films, a novel sensing mechanism has been proposed, with the direct participation of alkali ions.[28] For magnetite films, the high sensitivity may be due to the simultaneous presence of Fe^{+2} and Fe^{+3} ions in the materials, with charge jumping between these ions, enhanced by humidity.[29]

The high sensitivity of the films heated to 200 °C may be attributed to the presence of an amorphous phase which still contains the residual organics, not yet decomposed at 200 °C. The heat treatment at 450 °C for 24 h allows the formation of crystalline ilmenite-like $CdTiO_3$. The humidity-sensitive conduction mechanism for these films is of the ionic type. Their response is thus very limited, because the specific surface area of the materials is not enhanced by the presence of pores.

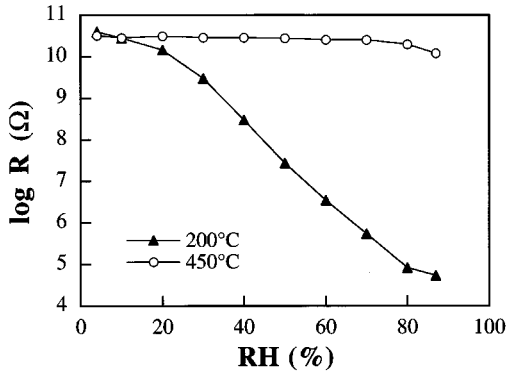

Figure 15 The RH dependence of the resistance of thin films heated to 200 °C and 450 °C, measured at 40 °C.

CONCLUSIONS

$CdTiO_3$ was prepared by the sol–gel method, in both its crystalline forms. XRD and Raman analyses confirmed the formation of the ilmenite–type phase (not ferroelectric) and its evolution with temperature into the perovskite-type structure (ferroelectric).

$CdTiO_3$ films (mono- and multi-layered) were prepared for their potential applications in electronics. Homogeneous and transparent films were obtained on various kind of substrates (glass, quartz, aluminium and steel), with different thicknesses. Ellipsometric measurements allowed the determination of their refractive index and thickness, as a function of temperature and of the crystalline phases formed within the deposit.

The humidity-sensitive electrical properties showed that the $CdTiO_3$ films in the ilmenite-type structure were not sensitive to relative humidity, while films which still contain the residual organics showed a response of as much as six orders of magnitude over the whole RH range tested.

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