JOURNAL OF MATERIALS SCIENCE **35** (2000) 5295–5299

Synthesis and characterization of cadmium titanium oxide powders by sol-gel technique

A. R. PHANI*,†, M. PASSACANTANDO, S. SANTUCCI
Department of Physics & Unità INFM, University of L'Aquila, Via Vetoio, Coppito, L'Aquila-671000, Italy
E-mail: rpa@cisunix.unh.edu

Uniform crystals of $CdTiO_3$ orthorhombic phase have been preapred by Sol-Gel method using titanium butoxide and cadmium acetate. For the first time the sample has been characterised detailedly to confirm the formation of pure single phase of $CdTiO_3$. It is observed that the sample sintered at 500°C for 5 h showed complete formation of the single phase of $CdTiO_3$ by X-ray diffraction technique. X-ray photoelectron spectroscopy measurement has been carried out for the bulk $CdTiO_3$ sintered at 500 °C for 5 h, which showed 20% of Cd, 20% of Ti and 60% of O indicating stoichiometric $CdTiO_3$. Surface morphology studies by scanning electron microscopy showed uniform crystals of $CdTiO_3$. The purity of the compound has also been checked by Energy Dispersive X-ray method indicating the absence of foreign ions apart from that, the ratio of Cd : Ti has been calculated and found to be 1 : 1 indicating the stoichiometric $CdTiO_3$.

1. Introduction

In recent years, there has been growing interest in Cadmium Titanium Oxide ($CdTiO_3$) as a possible new material for Optical fiber [1–3] and as a sensor material for the detection of NO_2 gas [4–6] applications. In order to replace other materials, pure and high quality with uniform crystals of $CdTiO_3$ of good optical quality are needed. Generally, it has been found that reaction sintering is difficult to control, especially when a chemically homogeneous, single phase product with high purity high density and uniform microstructure is desired. Sol-Gel processing has been investigated extensively as an alternative to conventional processing [7, 8], because of the oppurtunity for finer scale mixing, lower densification temperatures and ultimate improved properties. In particular, the sol-gel preparation method has gained much interest as a means to obtain ceramic materials at low temperature. Control of the microstructure has to be excercised when preparing this ceramic, because the microstructure is important when this is used as sensor material. This method inviolves the controlled hydrolysis of an alkoxide, followed by condensation, which in turn, forms a gel. The structure of the final compound or material is very sensitive to pH, stability of the reactants, amount of water, and impurities. In the present investigation work, we describe the synthesis of $CdTiO_3$ powders with orthorhombic phase using a Sol-Gel technique, which leads to high purity polycrystalline powders at temperatures lower than those used in solid state reactions.

2. Experimental procedure

All reagent garde chemicals (Aldrich) employed in the preparation procedure were used without further purification. cadmium acetate dihydrate and Titanium butoxide were used as Cadmium and Titanium sources. For the synthesis of $CdTiO_3$ in aqueous solution, a sol-gel reaction with ethylene glycol was used. A schematic flow chart diagram of the synthesis of $CdTiO_3$ powders has been shown in the Fig. 1. Stoichiometric amounts of cadmium acetate was dissolved in pure ethanol solvent in a two neck flask. To the above, 10 ml of ethylene glycol was added drop wise as a chelating agent. Titanium Butoxide was seperately dissolved in pure ethanol solvent which was addded to the above and the contents are stirred for 5 h to obtain homogeneous solution in a dry N_2 atmosphere. Then sufficient amount of distilled water is added to complete the hydrolysis. The contents are filtered, dried at 150°C for 24 h. The dried powder is ground in an agate mortar and pestle and the then passed through a 150 mesh sieve to eliminate any large agglomerates. Cylindrical compacts (10 × 6 mm) are prepared by die pressing at a pressure of 1 ton\cm^2. Sintering of cylindrical compacts are carried out in air at constant heating rate 2 °C/min, at 400 °C and 500 °C temperatures for 5 h. The sintered pellets have been ground in agate mortar and pestle to fine powder and analyzed by XRD, EDX, XPS and SEM techniques to find out phase formation, elemental analysis, composition and morphology respectively.

* Author to whom all correspondence should be addressed.
† *Present Address*: Mechanical Engineering Department University of New Hampshire, Durham, New Hampshire 03824 USA.

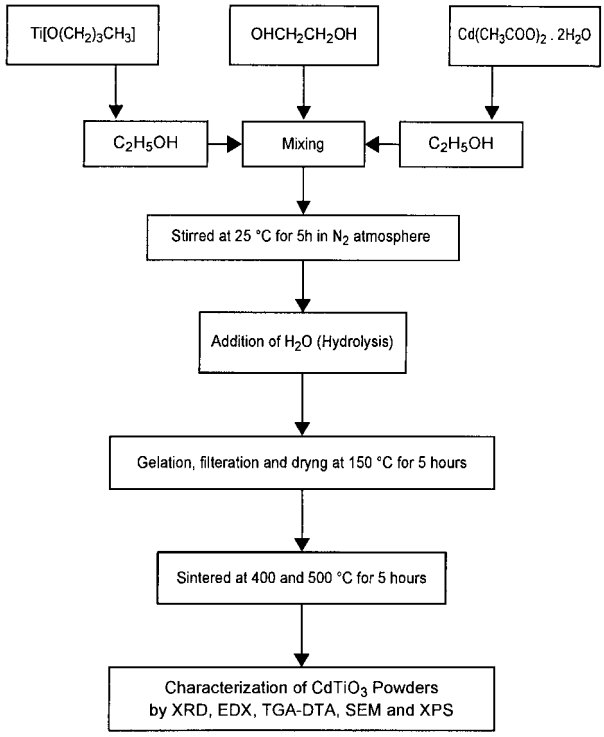

Figure 1 Schematic flow chart of the synthesis of the $CdTiO_3$ powders by Sol-Gel technique.

3. Results and discussions

3.1. X-Ray diffracttion

X-ray diffraction (XRD) (model: SIEMENS D5000) with copper target, K_α radiation ($\lambda = 1.5406$ Å) is used for phase identification where the diffracted intensities are recorded as a function of 2θ. The XRD pattern of the $CdTiO_3$ powder sintered at 400°C for 5 h has been shown in the Fig. 2a. This spectrum clearly shows the formation of $CdTiO_3$ is not completed at a sintering temperature of 400°C, showing broad peak of $CdTiO_3$ indicating the amorphous behavior of the phase. Fig. 2b shows the formation of single phase of $CdTiO_3$ at sintering temperature of 500°C for 5 h. The effects of sintering temperature on crystallographic structure and crystallite size for the samples sintered at 400°C and below (not shown here) revealed low intensity and broad peaks indicating the crystallinity is not well defined. On the other hand, sharp and intensive peaks are observed for the sample sintered at 500°C for 5 h, indicating a higher degree of crystallinity. For the sample sintered at 500°C for 24 h, all the diffraction lines agree with reported values and match with the JCPDS data (card No: 29–277) confirming the formation of rhombohedral $CdTiO_3$ structure. From the spectra the lattice parameters have been calculated and found to be $a = b =$ 5.235 Å, $c = 11.924$ Å which are in good agreement with the reported values from the JCPDS data. The crystallite size is calculated and found to be 706 Å by Scherrer formula applied to the (111) orientation which is the maximum reflection of the rhombohedral structure of $CdTiO_3$ at $2\theta = 31.5°$.

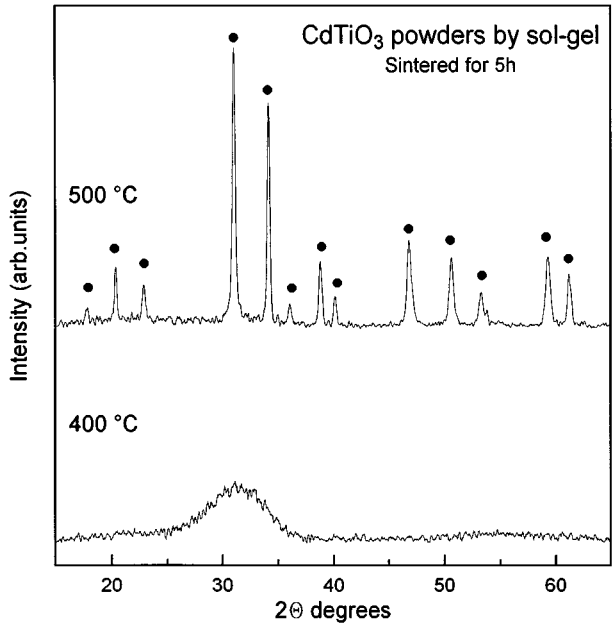

Figure 2 X-ray diffraction spectra of $CdTiO_3$ powders sintered at 400°C and 500°C for 5 h.

3.2. Thermogravimetric and differntial thermal analysis

Thermo-gravimetric analysis and Differential Thermal Analysis of the sample sintered at 500°C for 5 h has been carried out to determine the weight loss as well as the exact temperature for the formation of $CdTiO_3$. The Differential Thermal Analysis (DTA) and Gravimetric analysis (TGA) curves for $CdTiO_3$ powder in the temperature range 20°–1200°C at a heating rate of 10°C min^{-1} are shown in the Fig. 3. The TGA curve indicates that there is a initial weight loss of −7% followed by another −3%, immediately followed by −15% weight loss. This may be attributed to weight loss of H_2O Ethanol, and organic molecules respectively, which occurred at 100°C, 300°C respectively. Further, no weight loss has been observed between 400°C to 1200°C. On the other hand, we have observed three exothermic and three endothermic peaks in DTA spectrum. These are attributed to removal of H_2O and removal of organic molecules from the compound at 100°C and 300°C respectively. The formation and crystallization of $CdTiO_3$ phase has been confirmed by looking at the broad exothermic peak extending from

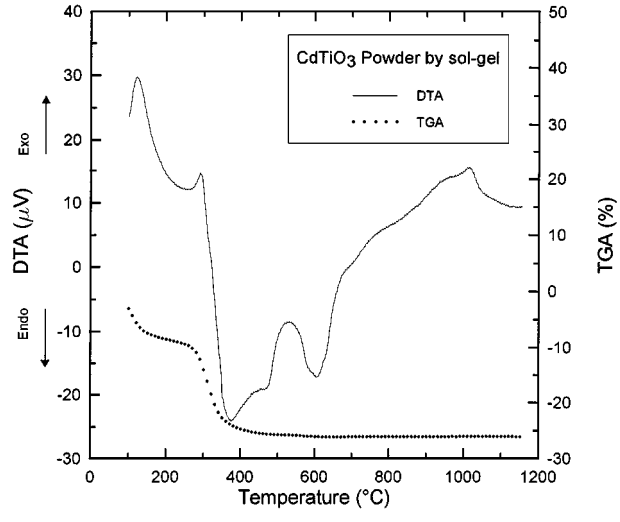

Figure 3 TGA and DTA spectra of $CdTiO_3$ powder.

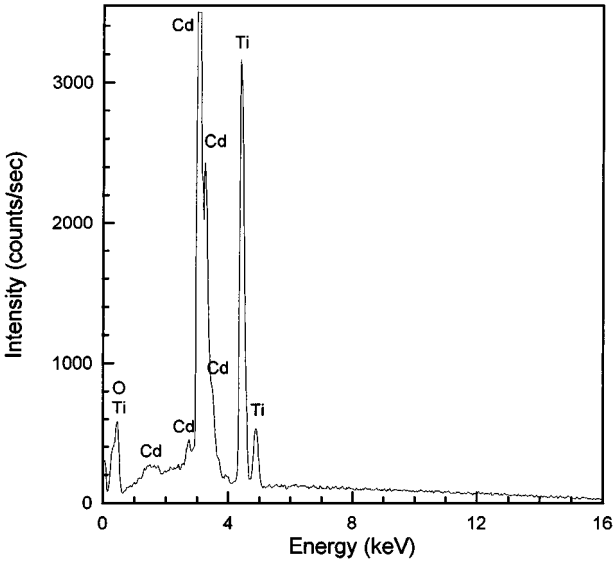

Figure 4 Energy Dispersive X-ray Analysis of pure $CdTiO_3$ powder sintered at 500°C for 5 h.

490°C to 590°C. This has been further confirmed by the X-ray diffraction technique for the same sample sintered at 500°C for 5 h in which, we have observed the formation of single phase of $CdTiO_3$.

3.3. Energy dispersive X-ray analysis

Energy Dispersive X-ray Analysis (EDX) has been carried to find out the elemental analysis for the sample sintered at 500°C for 5 h as shown in the Fig. 4. The spectrum shows the presence of Cd, Ti and O, indicating the purity of the compound. The ratio of Cd and Ti has been calculated and found to be 50% and 50% respectively, when compared to 50% and 50% of Cd and Ti in stoichiometric $CdTiO_3$.

3.4. Scanning electron microscopy

Fig. 5 shows the scanning electron micrographs of bulk $CdTiO_3$ samples after sintering at 400°C and 500°C for

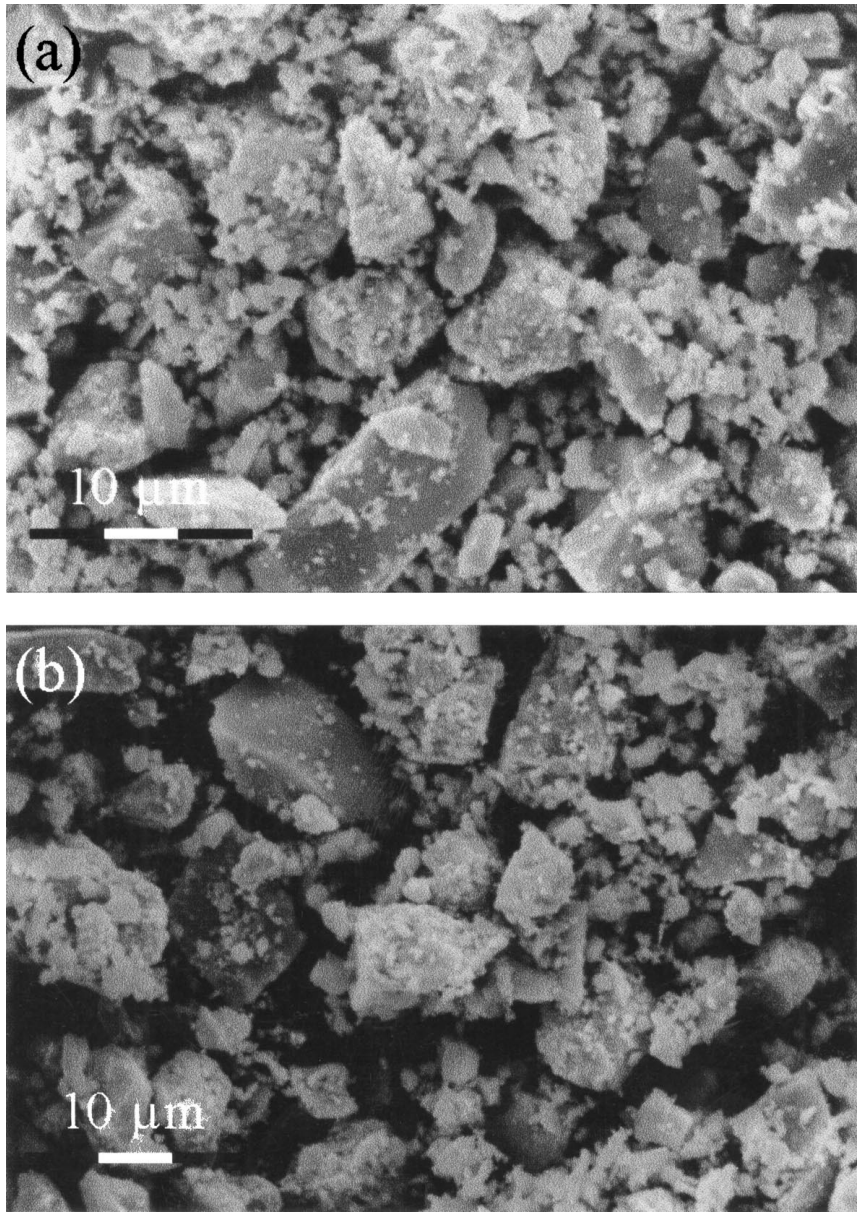

Figure 5 Scanning Electron Microscopy pictures of $CdTiO_3$ powders sintered at different temperatures for 5 h a) 400°C b) 500°C.

5 h respectively. The effect of sintering temperature on crystallite size for the sample sintered at 400°C for 5 h, reveals the formation of small crystals of $CdTiO_3$ along with un-reacted CdO and TiO_2 indicating the crystallinity of $CdTiO_3$ is not well defined. On the other hand, for the sample sintered at 500°C for 5 h shows that well crystallization of $CdTiO_3$ with uniform crystal size.

3.5. X-Ray photoelectron spectroscopy

X-ray photoelectron spectroscopy studies of the samples sintered at 400 °C and 500 °C for 5 h have been performed using the PHI ESCA system equipped with an Al K_α photon source ($h\nu = 1486.6$ eV) and a concentric hemispherical analyzer. Fig. 6 shows the survey scan acquired in the range of 0-1100 eV of the powders $CdTiO_3$ sample sintered at different temperatures. No contaminant species are detectable within the sensitivity of the technique. Only a small amount of adsorbed carbon is present on the spectra. This peak was used to calibrate the acquired spectra, and the position of the C 1s peak was located at binding energy (BE) of 284.5 eV [9]. Figs 7–9 shows the XPS of Cd 3d, Ti 2p and O 1s core level spectra. From the detailed spectra of the Ti 2p, Cd 3d and O 1s peaks, we obtained the exact composition of the compound, by calculating the atomic concentration of the individual species using the sensitivity factors [9]. We have found 1 : 1 for Cd and Ti indicating the stoichiometric composition of $CdTiO_3$ for both the sintered samples.

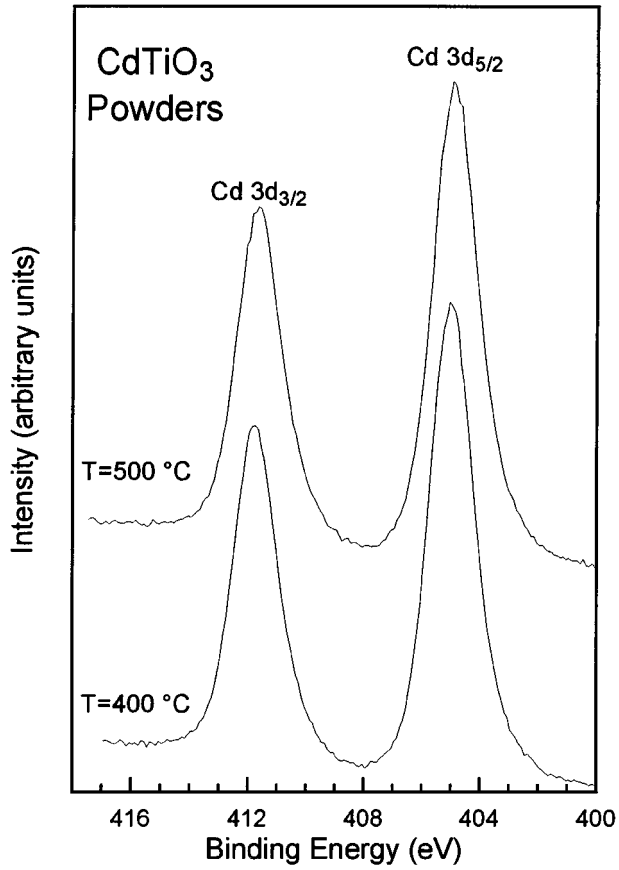

Figure 7 XPS of Cd 3d core level spectra of $CdTiO_3$ powders sintered at 400°C and 500°C.

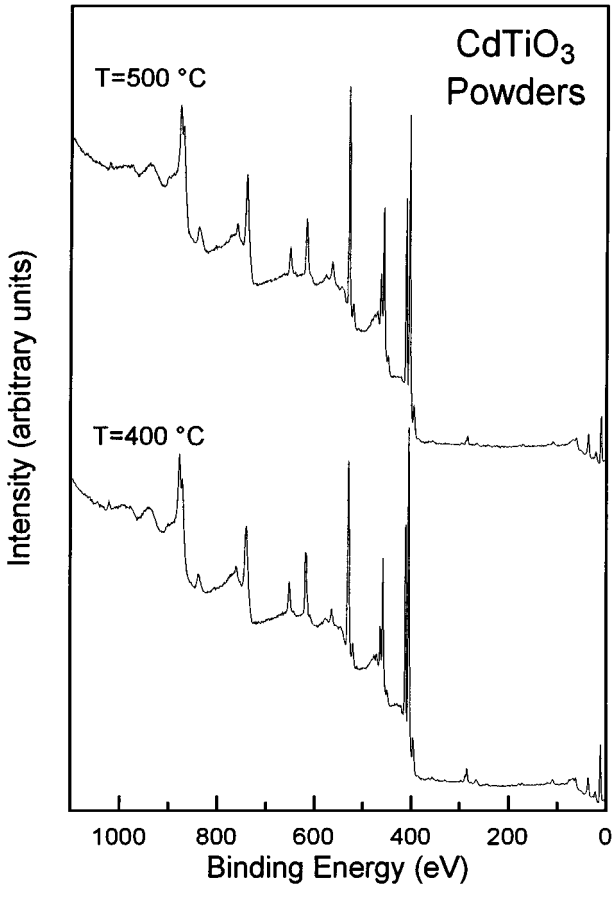

Figure 6 X-ray photoelectron spectroscopy survey scan of $CdTiO_3$ powders sintered at 400°C and 500°C.

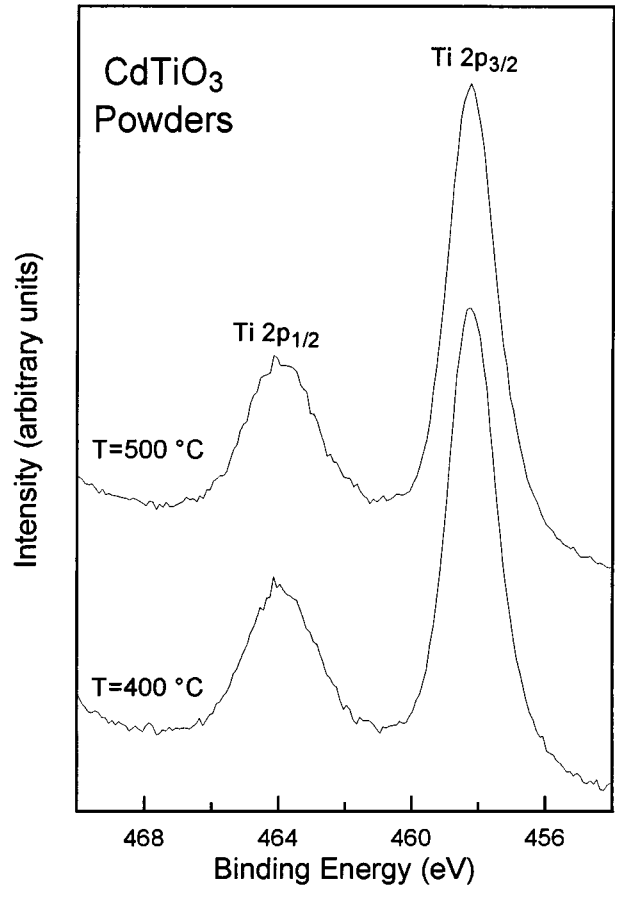

Figure 8 XPS of Ti 2p core level spectra of $CdTiO_3$ sintered at 400°C and 500°C.

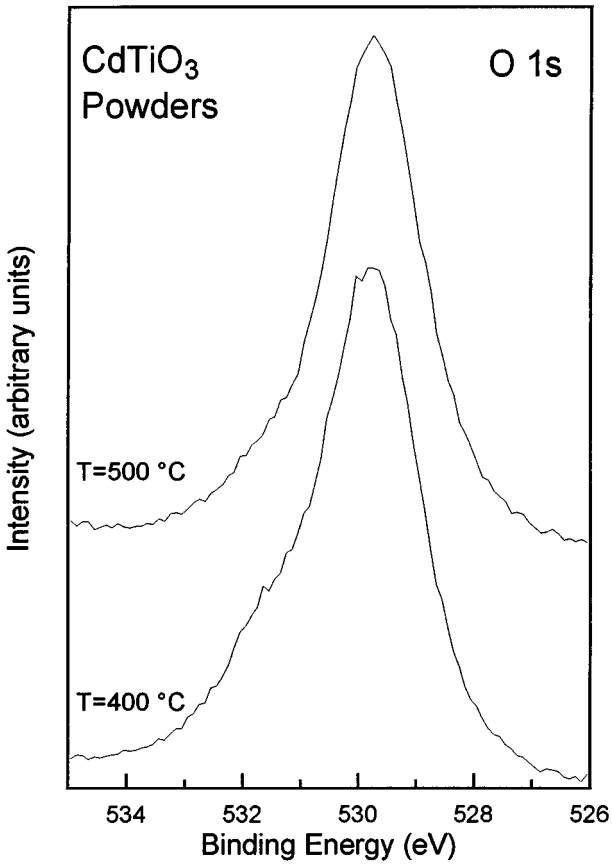

Figure 9 XPS of O 1s core level spectra of $CdTiO_3$ sintered at 400°C and 500°C.

4. Conclusions

In conclusion, we have synthesised high purity bulk single phase $CdTiO_3$ from Sol-Gel technique. The formation of this single phase has been confirmed by X-ray diffraction for the sample sintered at 500 °C for 5 h. The purity of the compound is confirmed by energy dispersive X-ray analysis as well as X-ray photoelectron spectroscopy studies indicating the absence of foreign ions and the exact percentages of composition, 20% of Cd, 20% of Ti and 61% of O in the bulk $CdTiO_3$. For the sample sintered at 500°C for 5 h. Scanning electron microscopy pictures of $CdTiO_3$ powders sintered at 500°C for 5 h reveals the uniform rock like structures.

Acknowledgements

The authors are thankful to Dr. C. Cantalini and Mrs. L. Prosperi for performing DTA/TGA measurements.

References

1. B. D. FADES, B. J. ZELINSKI and D. R. UHLMANN, "Ceramic. Films and Coatings," edited by J. Wachtmann and JR. A. Haber (Noyes Publications, Park Ridge, NJ, 1993) p. 224.
2. H. DISLICH, "Sol. Gel Technology for Thin Films, Fibers, Preforms, Electronics and Speciality Shapes," edited by L. C. Klein (Noyes Publications, Prak Ridge, NJ, 1993) p. 50.
3. R. B. PETTIT, C. S. ASHLEY, S. T. REEDAND and C. J. BRINKER, "Sol. Gel Technology for Thin Films, Fibers, Preforms, Electronics and Speciality Shapes," edited by L. C. Klein (Noyes Publications, Prak Ridge, NJ, 1993) p. 80.
4. T. BEIN, K. BROWN, G. C. FYE and C. J. BRIKER, *J. Amer. Cer. Soc.* **111** (1989) 7640.
5. Y. YAN and T. BEIN, "Interfacial Design and Chemical Sensing," Edited by T. E. Mallouk and D. J. Harrison (American Chemical Scoiety, Washington., D.C., 1994) p. 16.
6. A. R. PHANI, M. PASSACANTANDO, S. SANTUCCI and C. CANTALINI, *Thin. Solid. Films*, Unpublished.
7. A. R. PHANI, S. DI NARDO, M. PASSACANTANDO, L. LOZZI, S. SANTUCCI and C. CANTALINI, *J. Mat. Sci.* **33** (1998) 3969.
8. A. R. PHANI, M. PASSACANTANDO and S. SANTUCCI, *ibid.* Unpublished.
9. "Hand Book of X-Ray Photoelectron Spectroscopy," edited by J. Castain (Perkin-Elmer Corp, Een Praire, Minnisota 55344, USA).

Received 8 November 1999
and accepted 8 March 2000