

Bismuth vanadate synthesis by metallo-organic decomposition: thermal decomposition study and particle size control

A. GALEMBECK*, O. L. ALVES

LQES—Laboratório de Química do Estado Sólido, Instituto de Química, UNICAMP,
CP 6154, 13083-970 Campinas—SP, Brazil

E-mail: andre@npd.ufpe.br

E-mail: lqes@iqm.unicamp.br

Polycrystalline bismuth vanadate, BiVO_4 , was synthesized by metallo-organic decomposition (MOD), starting from bismuth 2-ethyl-hexanoate and vanadium (IV) oxy-acetylacetonate solutions in an organic solvent. The pyrolysis of the precursors at 500°C lead to single-phase samples, with particle sizes ranging from 0.65 to $1.40\ \mu\text{m}$, depending upon the heating time. The activation energies for the thermal decomposition of the precursors were estimated as 100.0 kJ/mol and 90.5 kJ/mol for bismuth and vanadium precursors, respectively. The method allows for the synthesis of powdered polycrystalline and/or thin film samples and may provide a route to doped/substituted compounds with minimal changes in the experimental procedures. © 2002 Kluwer Academic Publishers

1. Introduction

Bismuth vanadates can be prepared over a wide composition range, with remarkably different stoichiometries and structures. A phase diagram for the Bi : V : O system has been reported by Toubon and Vachon [1].

BiVO_4 based yellow pigments are potential substitutes for lead and cadmium based paints, due to their simultaneous high performance and problem-free ecotoxicological behavior. The high performance is a result of their brilliant clean, greenish-yellow shade, very high opacity and color strength. These vanadates also display an excellent price/performance ratio and a high durability, compared to competing organic pigments [2]. They present monoclinic structures with a reversible ferroelastic transition near 255°C to the tetragonal form. This phase transition leads to a pronounced thermochromic behavior. The tetragonal polymorph can be stabilized at low temperatures by several metallic cations, permitting control over the color properties according to the kind and amount of added metal [3]. BiVO_4 can also be used to oxygen separation, acting as a photocatalyst under the action of visible light [4].

Polycrystalline BiVO_4 with a controlled particle size distribution and shape is usually obtained by solid state reactions, at temperatures over 600°C [2, 5], or by sol-gel [6, 7]. Monocrystals may be grown by the Czochralski method [3].

Other important bismuth-vanadium based compounds are those called BIMEVOX, derived from $\text{Bi}_4\text{V}_2\text{O}_{11}$, in which the vanadium (V) ion is substituted by other metallic cations [8–10]. They present a strong

polar response and a high oxide ion conductivity near 770 K, which makes them attractive for application as a gas sensor [11] and in catalysis [12]. They are also under investigation as a potential solid electrolyte for the electrochemical separation of oxygen from air [8]. The high temperature $\gamma\text{-Bi}_4\text{V}_2\text{O}_{11}$ form can be stabilized at room temperature if vanadium is substituted by cations like Li^+ , Pb^{4+} and Al^{3+} [13].

More recently, some authors have proposed alternative routes for the preparation of these bismuth-vanadium based ceramics: (i) rapid microwave-assisted solid-state synthesis allowing substitution at vanadium sites by species like Ag^+ , Mn^{4+} and Y^{3+} [13, 14]; (ii) ball-milling of stoichiometric mixture of Bi_2O_3 and V_2O_5 , which leads to nanocrystalline powders [15] and (iii) reaction of layered potassium vanadate with bismuth nitrate, in an aqueous media, at room temperature [4].

Recently we have reported a route to BiVO_4 thin film deposition by the metallo-organic decomposition (MOD) process [16]. Barreca *et al.* here reported $\text{Bi}_4\text{V}_2\text{O}_{11}$ thin film preparation by chemical vapor deposition (CVD) [17].

The MOD technique involves the dissolution of the precursors in the desired stoichiometric ratio to obtain a true solution. This solution is deposited on a solid substrate by spray-, dip- or spin-coating and the wet film is heated at moderate temperatures to allow for solvent evaporation. A further heat treatment at higher temperature leads to pyrolysis of the precursors and crystallization of the inorganic solid. It is possible to

* Present Address: Departamento de Química Fundamental/CCEN, Universidade Federal de Pernambuco, CEP 50740-540, Recife, PE, Brazil.

modulate oxygen stoichiometry, particle size and film thickness [18]. The method has been applied to the synthesis of several materials like ferroelectrics [19, 20], superconductors [21] and transparent conductors [22].

In this work, we present use of the MOD technique for the synthesis of highly polycrystalline, particle size controlled BiVO_4 and a thermal decomposition study of the precursor compounds.

2. Experimental

Bismuth 2-ethyl-hexanoate, $\text{Bi}(\text{hex})_3$, (Strem Chemicals) and vanadium (IV) (oxy)acetylacetonate, $\text{VO}(\text{acac})_2$, synthesized according to the procedure described by Rowe and Jones [23], were dissolved separately in freshly distilled acetylacetonone and mixed in a stoichiometric ratio of $\text{Bi}/\text{V} = 1$. The green solution which resulted from mixing the individual precursor solution was homogenized for one hour and submitted to a heat treatment at 120°C until nearly 90% of the solvent was evaporated. This mixture was pyrolysed at temperatures ranging from 400 to 500°C for 2 to 15 h, leading to yellow solids.

The thermal decomposition experiments of the precursors were carried out using thermogravimetric analysis (TGA, Shimadzu 50-WS) at 5, 10, 15 and $20^\circ\text{C}/\text{min}$ heating rates, under 50 mL/min air flow. X-ray diffraction (XRD, Shimadzu XD-3A) of resulting powder samples were performed using $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) with 30 kV, at a $2^\circ/\text{min}$ rate. Raman spectroscopy (Renishaw U-3000 spectrometer) measurements were carried out with a 632.8 nm He-Ne laser and chemical analysis by X-ray fluorescence (XRF, Tracor Spectrace 5000) used the fundamental parameters method. Scanning electron microscopy (SEM) micrographs were obtained in a Jeol, model JSM T-300, microscope from gold coated dispersed powder samples.

3. Results and discussion

3.1. Thermal decomposition studies

The thermograms for each of the precursors and of the $\text{Bi}:\text{V}$ (1:1) mixture after solvent evaporation are shown on Fig. 1. The decomposition is complete at 350°C for $\text{Bi}(\text{hex})_3$ and 380°C for $\text{VO}(\text{acac})_2$ (Fig. 1a and b). The $\text{Bi}(\text{hex})_3$ residue was about 32.0%, a value

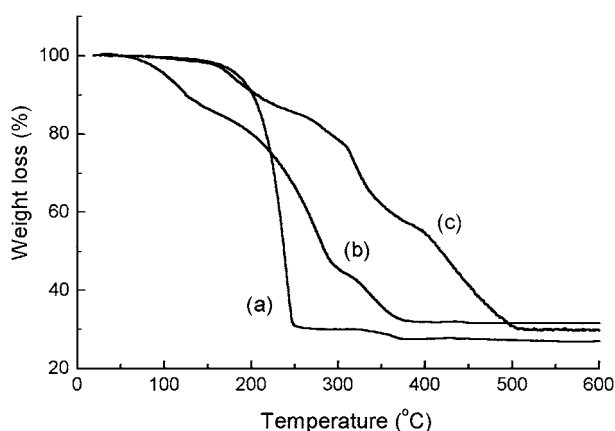


Figure 1 Thermogravimetric analysis. (a) $\text{Bi}(\text{hex})_3$; (b) $\text{VO}(\text{acac})_2$; (c) $\text{Bi}(\text{hex})_3 + \text{VO}(\text{acac})_2$ ($\text{Bi}/\text{V} = 1$) mixture after solvent evaporation.

consistent with Bi_2O_3 being the final product. The bismuth precursor showed three weight loss events. The first one ($\sim 9.9\%$) was attributed to the elimination of the stabilizer, whose amount is about 9%, according to the supplier. The second and third events correspond to the loss of 38.5% and 19.6% respectively. The expected value for the elimination of one 2-ethyl-hexanoate group is 20.0%. So, we can state that the $\text{Bi}(\text{hex})_3$ thermal decomposition proceeds with the elimination of two ligands simultaneously, up to 290°C , followed by the loss of the third one at about 350°C .

The vanadium precursor presented a 79.00% weight loss, which is higher than the expected value, 68.13%, for a V_2O_5 residue. Generally, β -diketonate complexes tend to sublime to some extent and, for this reason, are used with advantage as precursors in chemical vapor deposition. This fact did not cause problems in the BiVO_4 thin film deposition [16]. On the contrary, the synthesis of powder samples using the same procedure cannot be applied and will be discussed later.

The decomposition of the $\text{Bi}:\text{V}$ mixture is complete at nearly 500°C , a temperature above to those observed for each of the individual precursors (Fig. 1c). This provides important information to establish the conditions for the pyrolysis step. Also, the weight loss events observed in this thermogram showed a profile very distinct from that presented by the bismuth and vanadium compounds. This is evidence that there is some kind of interaction between the precursors during their thermal decomposition, which is desirable if one is interested in the synthesis of a $\text{Bi}-\text{V}$ mixed compound as a single phase [23, 24].

The TGA data were used also to estimate the activation energy (E_a) involved in the decomposition of the precursors by the Ozawa method [25]. The method is based on thermal analysis data collected with different heating rates and it is valid if the resulting curves can be superposed by a lateral shift. The length of the lateral shift is proportional to the logarithm of the corresponding experimental heating rate.

The basic approach is to plot the reciprocal absolute temperature for a given value of weight loss, measured for each heating rate. This should give a straight line, whose slope is the activation energy. If the weight loss event results from two or more activation energies, that are parallel or consecutive reactions, the curves will not be superposed and the analysis does not apply.

Another approach is to consider one of the curves as a master curve and plot the difference in the logarithm of heating rate against the distance of the lateral shift, that is the dislocation of the reciprocal absolute temperature relative to this master curve [26].

The calculations were performed using these two methods, with the intent to estimate the activation energy for the decomposition of $\text{Bi}(\text{hex})_3$, $\text{VO}(\text{acac})_2$ and the $\text{Bi}/\text{V} = 1$ mixture and, also, for free 2-ethyl-hexanoic acid. The Bi/V mixture did not give superposable curves, hence the method is not valid. The results are listed in Table I.

Since the thermal decomposition of the bismuth precursor shows two weight loss events, the calculations were performed separately for each one. In the case of $\text{VO}(\text{acac})_2$, only the first event could be superposed

TABLE I Estimated activation energies for metallo-organic precursor decomposition and decomposition temperature range

Compound	E_a (kJ/mol) [25]	E_a (kJ/mol) [26]	Decomposition range at a 10°C/min heating rate (°C)
Bi(hex) ₃	44.06	42.38	125–290
	58.16	55.55	290–350
VO(acac) ₂	93.20	87.80	140–380
hexanoic acid	28.67	26.97	80–190

for all curves and, hence, for the second event (between 330°C and 390°C, with a 4.38% weight loss) the method cannot be applied. The two methods showed good agreement, with differences of less than 5%. The 2-ethyl-hexanoic acid presented one only weight loss event.

To the best of our knowledge, there is no published data regarding these compounds. Indeed, a 269 kJ/mol value was reported for BaCO₃ decomposition to yield the superconductor oxide YBa₂Cu₃O_{7-y} at 750°C [27].

The calculated activation energy was then used to estimate the reduced time, which is a kinetic parameter that allows theoretical prediction of the thermal behavior under other experimental conditions [28]. We used these data to calculate the Bi(hex)₃ and VO(acac)₂ thermal decomposition occurring isothermally at 200°C. The resulting graphs are presented in Figs 2 and 3.

Fig. 2 shows the calculated generalized time, θ , and a simulation for a 200°C isothermal decomposition versus the weight loss of the bismuth precursor. It is clearly seen how θ is independent of the experimental conditions as each weight loss event does not present any relationship. However, when a real situation is simulated, the resulting curve shows a typical thermogram profile.

The curve presented in Fig. 3a refers to the generalized time and the simulation of a isothermal heat treatment at 200°C for the vanadium precursor on the abscissa. We also plotted (Fig. 3b) the experimental thermogram in the same weight loss range against time, for comparison.

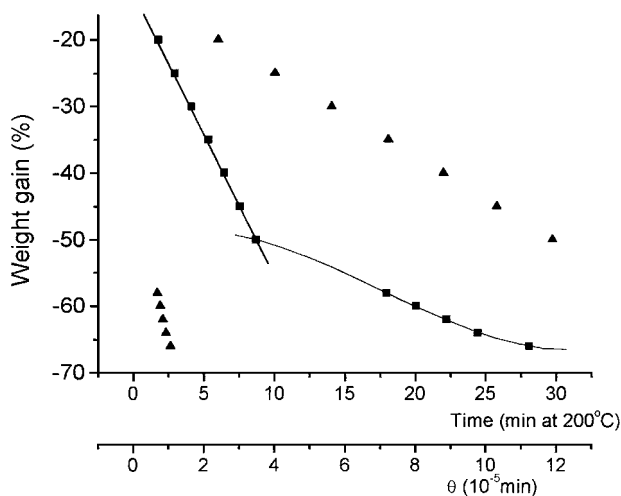


Figure 2 Weight loss against the calculated reduced time for Bi(hex)₃ thermal decomposition (▲) and a simulation for an isothermal heat treatment at 200°C (■).

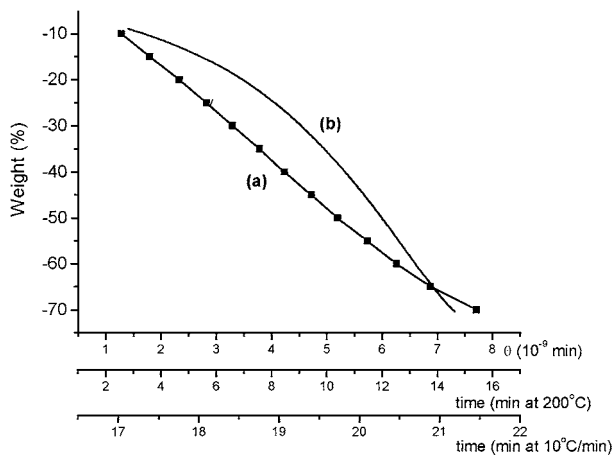


Figure 3 VO(acac)₂ thermal decomposition. (a) reduced time and simulation for an isothermal heat treatment at 200°C. (b) experimental thermogram for the same weight loss range.

This clearly illustrates that the sample treated isothermally, at lower temperature, should take more time to decompose, which supports the validity of the Ozawa method for the compounds studied here.

3.2. Powder formation

The heat treatment on the precursor mixture led to highly crystalline samples. Representative X-ray diffractograms are presented in Fig. 4. Attempts to obtain BiVO₄ by direct pyrolysis of the solution, without previous evaporation of the solvent, lead to a phase mixture composed of α -Bi₂O₃ and BiVO₄ (Fig. 4a). This was attributed to vanadium precursor loss by volatilization. The synthesis of BiVO₄ as a single phase (Fig. 4b) was successful only if the solvent was previously evaporated.

It is important to point out that the BiVO₄ is formed directly from the precursors, not through bismuth and vanadium oxide formation as an intermediate step. This situation is highly favorable for the MOD technique [18, 24]. This is consistent with the observation

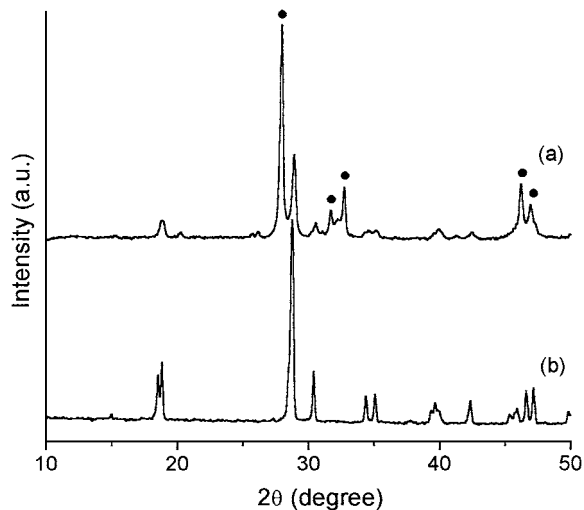


Figure 4 XRD diffraction of the precursor mixture (Bi/V = 1) heated at 500°C for 5 h. (a) without previous solvent evaporation: α -Bi₂O₃/BiVO₄ phase mixture; (b) after solvent evaporation: BiVO₄ (single phase). All unmarked peaks refer to BiVO₄. The (●) symbol refers to α -Bi₂O₃.

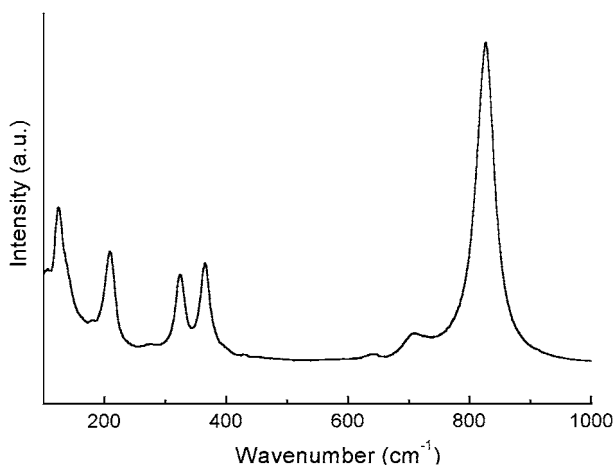


Figure 5 Raman spectrum of polycrystalline BiVO_4 . The sample were heated at 500°C for 5 h.

of the thermal behavior of the individual precursors and their admixture, as described above. Reversible thermochromic behavior was also observed for BiVO_4 samples.

The results of chemical analysis, obtained by X-ray fluorescence, are close to the theoretically expected values, with an error lower than 1%.

The single phase synthesis was also confirmed by Raman spectroscopy. The recorded spectra presented all bands described in the literature for this compound between 100 and 1000 cm^{-1} [29]. Polycrystalline powders and thin film samples synthesized by the MOD process showed nearly identical Raman spectra, as described in our earlier paper [16]. These spectra are dominated by an intense band near 820 cm^{-1} , assigned to the V-O symmetric stretching (A_1 species) for the tetrahedral VO_4 groups (Fig. 5).

Fig. 6 show scanning electron micrographs of BiVO_4 samples prepared at 500°C , with different heating times. Round shaped particles, nearly spherical or ellipsoidal are observed. The inset shows particles which are interconnected by “necks”, resembling a sintering process. It was verified that particle size may be controlled by changing heat-treatment time. Samples synthesized with 10 and 15 h heating times presented 0.65 and $1.40\text{ }\mu\text{m}$ average diameters, respectively.

It is also important to point out that the synthesis of single-phase bismuth vanadates is not an easy task. Interesting new routes have been proposed, such as the monomode microwave method, which permits the preparation of the sample in less than five minutes, leading to phase mixtures [14]. Also, CVD deposition of bismuth vanadates led to $\text{Bi}_4\text{V}_2\text{O}_{11}$ thin films, but BiVO_4 was obtained mixed with VO_2 [17].

The method presented here may be applied to any other Bi : V stoichiometric ratio and/or substituted with the insertion of other metallic cations, to synthesize substituted bismuth vanadates. This is possible because the precursors are initially mixed in a true solution, whose composition may be adjusted to the stoichiometric ratio desired for the final products.

4. Conclusion

The proposed route is very versatile as it permitted particle size control by changing only the heat-treatment time and may be used to incorporate other metallic cations with minimal change in the synthesis parameters. These features are highly desirable if one intends to apply the material as a yellow pigment.

Simple experimental conditions, stoichiometric control and dopant addition may be applied to synthesize

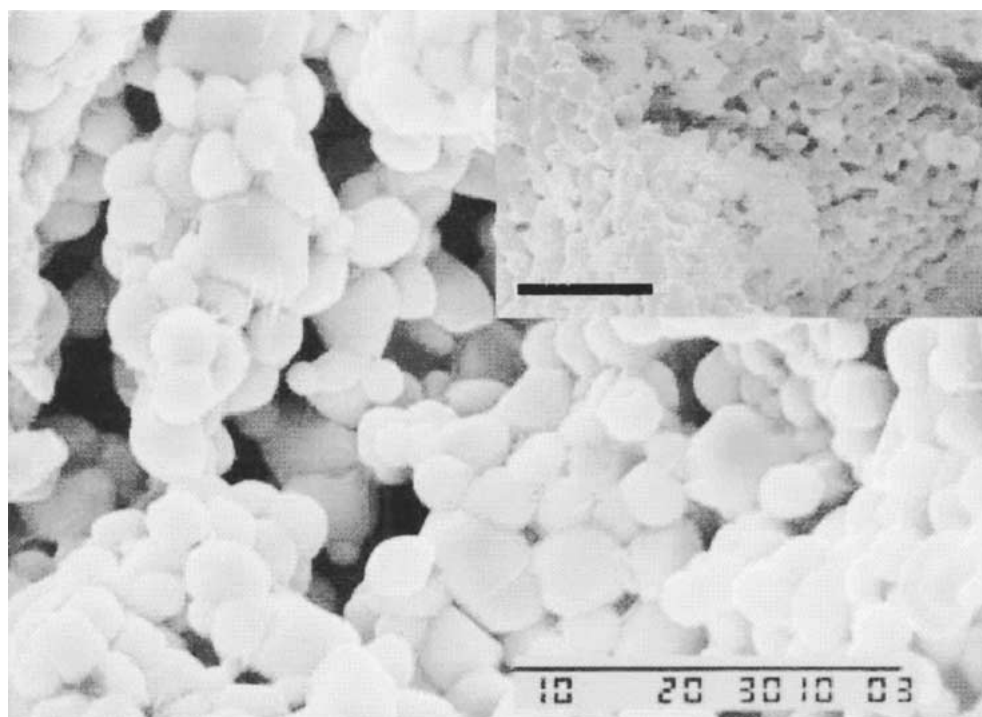


Figure 6 Scanning electron microscopy of a BiVO_4 sample prepared by heating the precursors at 500°C for 10 h. The inset refers to a heat treatment at the same temperature for 5 h. The scale bars refer to $10\text{ }\mu\text{m}$.

other Bi-V phases such as polycrystalline powdered solids or thin films.

References

1. M. TOUBON and C. VACHON, *Thermochim. Acta* **133** (1988) 61.
2. *The Bulletin of the Bismuth Institute* **70** (1997).
3. A. W. SLEIGHT, H. Y. CHEN and A. FERRETTI, *Mater. Res. Bull.* **14** (1979) 1571.
4. A. KUDO, K. OMORI and H. KATO, *J. Am. Chem. Soc.* **121** (1999) 11459.
5. M. E. MEDEIROS, Ph.D. thesis, UNICAMP, Brazil (1996).
6. K. HIROTA, K. KOMATSU, M. YAMASHITA, H. TAKEMURA and O. YAMAGUSHI, *Mater. Res. Bull.* **27** (1992) 823.
7. R. W. HESS, US Patent no., 41,151,142 (1978).
8. M. ANNE, M. BACMANN, E. PERNOT, F. ABRAHAM, G. MAIRESSE and P. STROBEL, *Physica B* **180/181** (1992) 621.
9. J. C. BOIVIN, C. PIROVANO, G. NOWOGROCKI, G. MAIRESSE, P. LABRUNE and G. LAGRANGE, *Solid State Ionics* **115** (1998) 639.
10. C. K. LEE and C. S. ONG, *ibid.* **117** (1999) 301.
11. P. B. AVAKYAN, M. D. NERSESYAN and A. MERZHANOV, *Am. Ceram. Soc. Bull.* **75** (1996) 50.
12. A. CHERRAK, R. HUBAUT, Y. BARBAUX and G. MAIRESSE, *Catal. Lett.* **15** (1992) 377.
13. B. VAIDHYANATHAN, K. BALAJI and K. J. RAO, *Chem. Mater.* **10** (1998) 3400.
14. M. GASGNIER, A. PETIT, M. F. GARDETTE, E. RIVIERE, S. LAUNAY, A. DWORKIN and S. TOSCANI, *J. Alloy Compd.* **309** (2000) 219.
15. K. SHANTHA and K. B. R. VARMA, *J. Mater. Res.* **14** (1999) 4651.
16. A. GALEMBECK and O. L. ALVES, *Thin Solid Films* **365** (2000) 90.
17. D. BARRECA, L. E. DEPERO, V. DI NOTO, G. A. RIZZI, L. SANGALETTI and E. TONDELLO, *Chem. Mater.* **11** (1999) 255.
18. R. W. VEST, *Ferroelectrics* **102** (1990) 53.
19. D. WU, A. D. LI, Z. LIU, H. LING, C. Z. GE, X. LIU, H. WANG, M. WANG, P. LÜ and N. B. MING, *Thin Solid Films* **336** (1998) 172.
20. Z. G. ZHANG, J. S. LIU, Y. N. WANG, J. L. ZHU, D. SU and H. M. SHEN, *J. Appl. Phys.* **85** (1999) 1746.
21. S. C. FANG, C. H. HUANG, I. C. CHEN, C. F. LIAW and W. M. HURNG, *J. Mater. Sci.* **29** (1994) 99.
22. Y. SAWADA, K. OMIKA, Y. ITO, F. MUTA and M. MOMOTA, *J. Thermal Anal.* **40** (1993) 1145.
23. R. A. ROWE and M. M. JONES, *Inorg. Synth.* **5** (1957) 114.
24. O. L. ALVES, C. RONCONI and A. GALEMBECK, *Quim. Nova* **25** (2002) 69.
25. T. OZAWA, *Bull. Chem. Soc. Jpn.* **38** (1965) 1881.
26. *Idem.*, *Thermochim. Acta* **124** (1988) 389.
27. A. NEGISHI, Y. TAKAHASHI, R. SAKAMOTO, M. KAMIMOTO and T. OZAWA, *ibid.* **132** (1988) 15.
28. T. OZAWA, *ibid.* **100** (1986) 109.
29. J. GHAMRI, H. BAUSSART, M. LE BRAS and J.-M. LEROY, *J. Phys. Chem. Solids* **50** (1989) 1237.

Received 24 October 2001
and accepted 30 January 2002