Effect of microstructure on the stability of nanocrystalline tin dioxide ceramics

Svetlana M. Kudryavtseva, Alexei A. Vertegel, Sergei V. Kalinin, Nikolai N. Oleynikov, Ludmila I. Ryabova, Leonid L. Meshkov, Sergei N. Nesterenko, Marina N. Rumyantseva and Alexander M. Gaskov*

Department of Chemistry, Moscow State University, 119899, Moscow, Russia

Powdered nanocrystalline tin dioxide has been prepared by two different methods: conventional hydrolysis of $SnCl_4$ solution and the so-called criosol technique. The latter involves treatment of a sodium stannate solution by a cation exchange resin in the H^+ form and subsequent freeze drying. The microstructure, composition, specific surface area and electrical properties of the samples were investigated. The application of the criosol technique was shown to result in stable nanoscale particles of tin dioxide. The sintered pellets obtained by this method are characterised by significantly higher values of the resistance in comparison to material prepared by the conventional technique.

At present thin films and ceramics based on nanocrystalline tin dioxide are widely used as materials for solid-state gas sensors.[1] One of the most important factors that influence the sensing properties of these materials is their microstructure. The best sensing characteristics are achieved when the grain size D is comparable to the thickness of the electron depletion layer L, which is determined by the Debye length and the oxygen chemisorption energy.[2] For tin dioxide ceramics the value of L was shown[3] to be *ca.* 3 nm and therefore the problem of synthesis of SnO_2 samples with nanoscale grain size is of special interest.

Although conventional precipitation results in samples characterised by nanometric grain size, the sintering of the as-prepared powders, which is necessary for the preparation of well defined material, leads to the substantial growth of the crystallites.[2] This problem can be avoided by the addition of foreign oxides that stabilise the size of the tin dioxide crystallites ($D \leqslant 10$ nm) even after annealing at 900 °C.[4,5] Another way to obtain SnO_2 with nanometric grain size stable to heat is the use of colloid systems as precursors ('sol–gel' technique). Several variants of the sol–gel method exist, however, only one of these, based on the hydrolysis of alkoxides, is usually applied for the synthesis of tin dioxide.[6] Other important factors that may influence the sensing properties of the material are the shape of the crystallites and the degree of agglomeration. These factors strongly affect the surface characteristics of the sample, such as porosity and specific surface area.[7–10] The above mentioned properties are also determined by the elaboration method used. Thus, there is a necessity for the development of SnO_2 synthesis techniques that lead to the possibility of controlling the microstructure of the sample.

In the present work we apply the newly developed criosol technique[11] for synthesis of nanoscale tin dioxide particles. The grain size, microstructure, specific surface area and electrical properties of SnO_2 obtained by this method are compared with samples prepared by conventional precipitation.

Experimental

The experiments were carried out with two tin dioxide powders (A and B) synthesised as shown in Fig. 1.

Powder A was prepared by conventional hydrolysis of $SnCl_4$. A measured amount of $SnCl_4 \cdot 5H_2O$ was dissolved in deionized water in an ice bath and liquid ammonia was slowly added to the stirred solution to achieve complete precipitation of α-stannic acid. The precipitate was centrifuged and washed with deionized water until the absence of chloride ion ($AgNO_3$ test). The precipitate was then dried at 100 °C for 24 h.

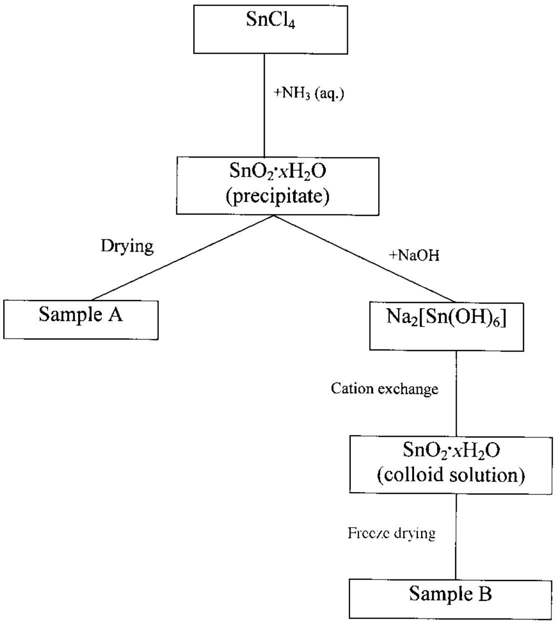

Fig. 1 Synthesis scheme

Powder B was prepared by means of the criosol technique.[11,12] Previously this method has been applied for the synthesis of Al_2O_3, Cr_2O_3 and Fe_2O_3. The technique is based on the pH-controlled treatment of an aqueous solution containing a multivalent metal nitrate by anion exchange with a resin in the OH^- form. Freeze drying of the colloid solutions results in the formation of an amorphous metal hydroxide that can be transformed to corresponding oxide by thermal dehydration. However, an attempt to treat the solution of $SnCl_4$ (0.01 M) by anion-exchange was unsuccessful: addition of the first portions of the ion-exchanger resulted in the formation of a precipitate.

In the present work we applied, for the first time, a treatment of an anionic hydroxo complex with a cation-exchange resin in the H^+ form. Sodium stannate was synthesised by reaction of α-stannic acid with 1 M sodium hydroxide. This solution was then diluted so that the concentration of $Na_2[Sn(OH)_6]$ was *ca.* 0.01 M. The solution was then treated with small (*ca.* 1 g) portions of a cation-exchange resin in the H^+ form and aged for 15 min after each cycle of the process in order to achieve hydrolytic equilibrium. The pH of the solution was controlled during of the treatment. The following reaction occurred during the cation exchange where Cat denotes the polymeric base of the ion-exchanger)

$$Na_2[Sn(OH)_6] + Cat{-}H \rightarrow SnO_2{\cdot}xH_2O + Cat{-}Na$$

The reaction yields a stable colloid solution of the tin acid ($pH = 6.5$) with no side-products. During the second step of the synthesis the colloid solution was subjected to freeze drying in a sublimator (SMH-15, Usifroid). This leads to a very friable SnO_2 powder ($\rho \approx 0.05$ g cm^{-3}).

Samples A and B were annealed at different temperatures (300–700 °C) for 24 h in air. The grain size of SnO_2 was measured by X-ray diffraction broadening analysis of the {110} and {101} lines. The average crystal size was estimated from Scherrer's equation. The surface area of the samples was determined by gas adsorption. The surface composition was investigated using Auger spectroscopy (JAMP-10 CCS JEOL) and the microstructure by scanning electron microscopy (2000FX JEOL). The samples were also characterised by thermogravimetry (TG) (Sinku-Riko ULVAC). Electrical conductance behaviour of the samples was studied in the temperature range 77–300 K. The measurements were carried out for the powders annealed at 300 °C (24 h), pressed into pellets at 700 MPa and sintered at 700 °C for 4 h.

Results and Discussion

The SEM micrographs shown in Fig. 2 demonstrate that the morphology of the A and B powders is quite different. Sample A consists of three-dimensional agglomerates with diameters of *ca.* 50 µm. In contrast, the crystallites of sample B are agglomerated in thin two-dimensional platelets. Since the platelets are transparent to the electron beam one can conclude that their thickness does not exceed 10 nm.

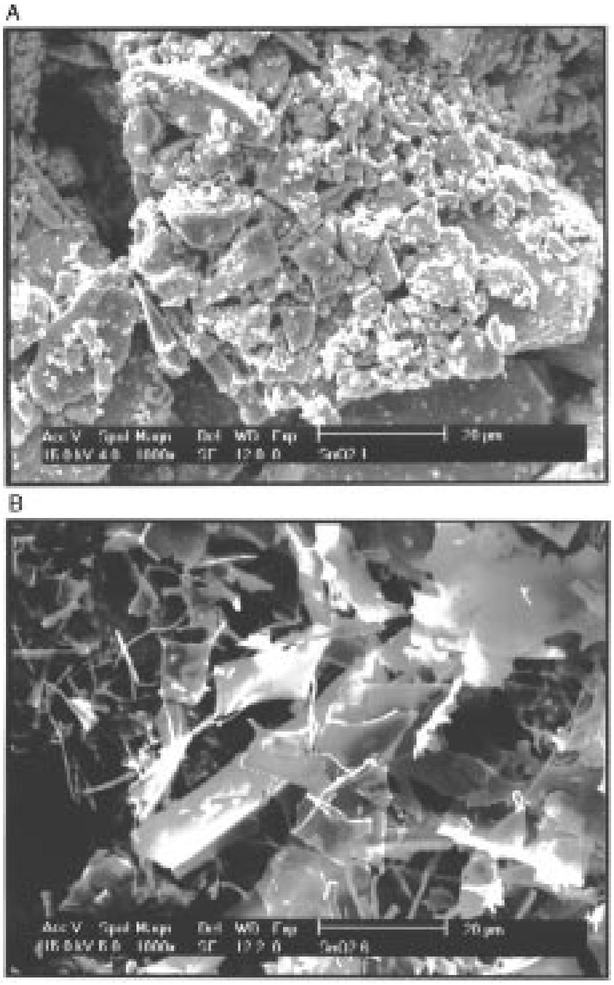

Fig. 2 SEM micrographs of the as-prepared samples A and B

This feature of the microstructure is probably connected with peculiarities of freezing of colloid solutions. Indeed, freezing in liquid nitrogen results in the formation of hexagonal ice that crystallises in thin platelets during the rapid growth. These crystallites probably act as a template for the following formation of SnO_2. It also should be noted that particles of aluminium and iron(III) oxides obtained by the criosol technique are also characterised by two-dimensional morphology.[13]

The X-ray data for the as-prepared samples A and B are presented in Fig. 3. One can see that the sample A synthesised by a conventional method is amorphous, while the diffraction spectrum of sample B obtained by the criosol technique contains very broad reflections of cassiterite.

The Auger spectra of the samples A and B demonstrate that both contain a small amount of chlorine (<1 atom%) that cannot be eliminated from the initial precipitate of α-stannic acid. In addition, sample B contains sodium on the grain surface that is probably adsorbed by colloidal particles during formation.

The water content of the samples A and B was analysed by TG (Fig. 4). The mass loss of the sample A (14.5%) is close to that of samples obtained by precipitation.[4] At the same time the water content in the sample B is 21.6%, which is probably due to the softer conditions of drying (T_{max} of the freeze-drying is +50 °C). However, it should be noted that both samples have a composition close to $SnO_2{\cdot}2H_2O$ (water content = 19.3%).

The change of the grain size D of SnO_2 crystallites with annealing time was studied by X-ray diffraction broadening analysis of the {110} and {101} reflections (Fig. 5). It should be noted that the grain sizes obtained for the different crystal planes of the same sample are very similar. Thus, we can conclude that the crystals have similar dimensions in all directions. One can see that the behavior of the samples A and B is quite different. The crystal size of sample A substantially grows during annealing (from 4 nm up to 20 nm after annealing

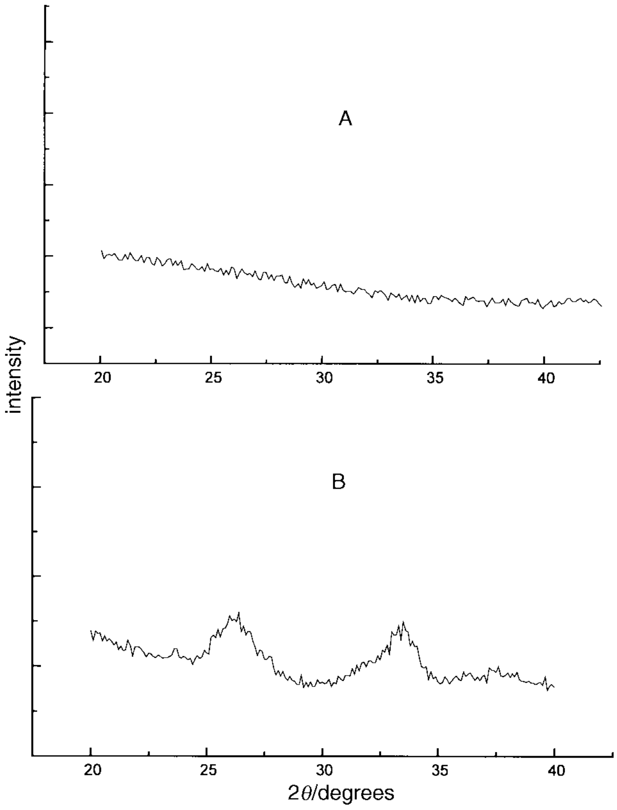

Fig. 3 X-Ray diffraction spectra of the as-prepared samples A and B

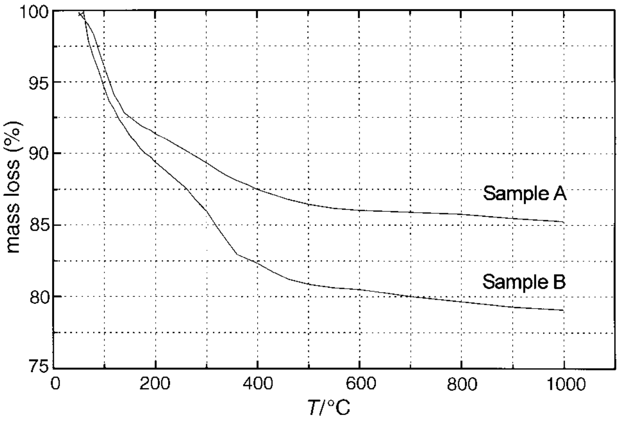

Fig. 4 Thermogravimetric analysis of samples A and B

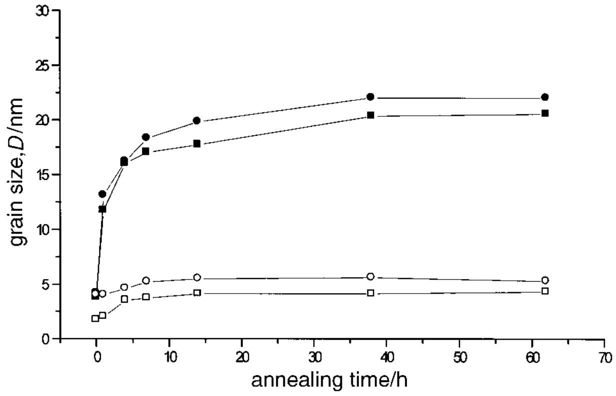

Fig. 5 Dependence of the grain size of samples A and B on the annealing time at $T = 600\,°C$: ■, A {110}; □, B {110}; ●, A {101}; ○, B {101}

for 60 h). Over the same time, the grain size of the sample B scarcely changes, and does not exceed 6 nm. Similar behavior was observed for the dependence of the grain size upon the annealing temperature (Fig. 6). Therefore, the application of cation exchange results in nanoscale particles of tin dioxide which are stable to heat.

The measurements of the specific surface area are in good agreement with X-ray diffraction data. The surface areas of the samples A and B annealed at 300 °C were approximately the same (*ca.* 70 $m^2\ g^{-1}$). However, the specific surface area of the sample A drastically decreases with the increase of annealing temperature (5 $m^2\ g^{-1}$ at 700 °C) while for sample B its value remains $>50\ m^2\ g^{-1}$ (Fig. 7).

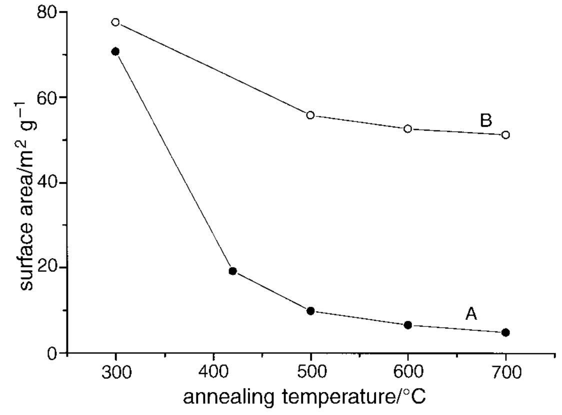

Fig. 7 Specific surface area of samples A and B as a function of annealing temperature

The large specific surface area and thermal stability of the sample B nanocrystallites can be explained from the theory suggested by Lifshits and Slezov.[14,15] According to their theory, a solid-state system with narrow particle size distribution develops during thermal treatment much more slowly than that characterised by a broad size distribution. This is related to the fact that the driving force of the crystal growth is determined by the difference between chemical potentials of the largest and the smallest particles. Thus, systems with a broad size distribution readily undergo recrystallization, while homogeneous systems are relatively inert even if they consist of very small particles (Fig. 8).

In the case of the criosol technique, the uniformity of the particle size is predetermined by the method of the synthesis. Ion exchange results in the formation of a restricted number of polymeric hydroxo complexes with nanometric sizes (primary particles), which are connected into colloidal aggregates by relatively weak bonds. Freeze-drying enables fixing of the structures prepared in colloid solution and these are converted into the solid state without significant change. Therefore, the solid-state system consisting of uniform primary particles should be stable to heat. Since the specific surface area is determined mainly by grain size, it also changes negligibly upon increasing the annealing temperature.

The main difficulty during electrical measurements is the problem of creation of ohmic contacts. Two types of contacts have been mounted: platinum wires pressed into the volume of the sample and silver layers deposited on the surface. Attempts to measure the resistance R of sample A pellets with different grain sizes were unsuccessful. The current–voltage characteristics (CVC) appeared to be significantly non-linear and unstable with variation of amplitude, sign and duration

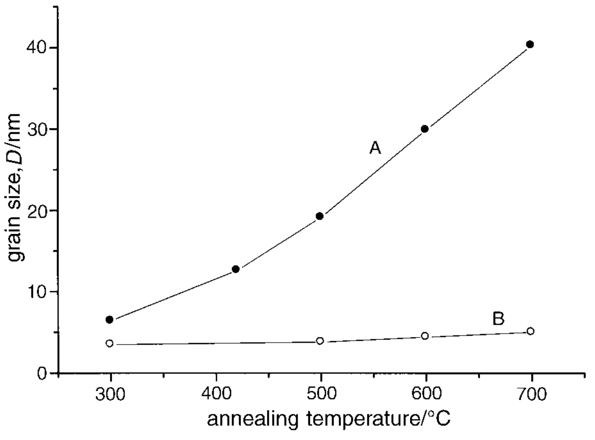

Fig. 6 Grain size of samples A and B as a function of annealing temperature

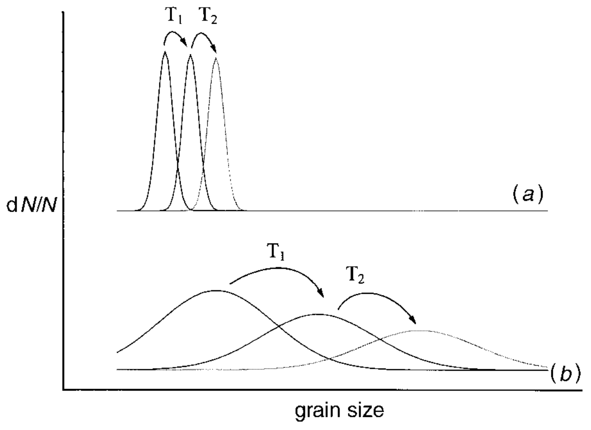

Fig. 8 Schematic plot of the evolution of solid state systems characterised by narrow (a) and broad (b) particle distribution functions during thermal treatment

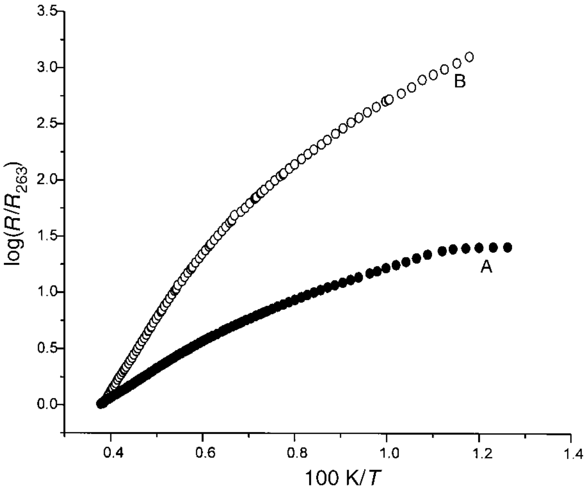

Fig. 9 Relative resistance as a function of temperature for samples A and B

of the current flow through the sample. These processes are probably due to the existence of a volume charge both in the contact regions and in the bulk of the samples. In particular the observed effects are likely to be connected to a significant amount of water absorbed in the pellets. Unstable behavior of CVC was also found for the samples sintered at high temperature with Pt contacts.

It was shown that only the application of silver contacts to the sintered samples enables reproducible values of the electrical resistance to be obtained. The signal measured from such contacts seemed to be stable at voltages <2 V with CVC being linear. The temperature dependence of the resistance was measured at a fixed voltage $U=1$ V. The experimental curves are shown in Fig. 9. Since the pellets are of slightly different size the relative values $R_r(T)=R(T)/R(263\ \text{K})=R/R_{263}$ are presented. At room temperature $R=2.3\times10^3$ and $2.6\times10^4\ \Omega$ for pellets of samples A and B, respectively. At high temperatures an activation region in $\log(R)$–$100/T$ plot is clearly observed for pellet B. The activation energy E_a estimated from the relation $R\approx\exp(E_a/kT)$ was *ca.* 130 meV. It should be mentioned that the experimentally determined value of E_a for pellet B is close to the activation energy of oxygen vacancies in SnO_2 single crystals.[16]

Comparison of the resistance values of pellets of samples A and B at different temperatures shows that pellet B, where the grain structure is nearly two-dimensional, is characterised by significantly higher values of resistance and stronger temperature dependence of R. Therefore, one can expect that samples obtained by the criosol technique will possess better sensing properties than those prepared by conventional precipitation (for examples, see ref. 17 and 18).

Conclusion

Tin dioxide powders have been prepared for the first time by a cation-exchange variant of the criosol technique. The synthesised powders contain particles with two-dimensional structure. X-Ray diffraction broadening analysis demonstrated that the criosol technique results in nanoscale particles of tin dioxide which are stable to heating. The samples obtained using the criosol method are characterised by higher specific surface area and significantly higher values of electrical resistance in comparison with those synthesised by conventional precipitation. The above mentioned properties indicated that the criosol technique may be of substantial interest for preparation of materials for tin dioxide-based gas sensors.

This work was partially supported by the Russian Foundation of Basic Research (grant No. 96-03-33122a).

References

1 W. Gopel and K. D. Schierbaum, *Sens. Actuators B*, 1995, **26–27**, 1.
2 C. Xu, J. Tamaki, N. Miura and N. Yamazoe, *Sens. Actuators B*, 1991, **3**, 147.
3 C. Xu, J. Tamaki, N. Miura and N. Yamazoe, *Electrochem. Soc. Jpn.*, 1990, **58**, 1143.
4 C. Xu, J. Tamaki, N. Miura and N. Yamazoe, *J. Mater. Sci.*, 1992, **27**, 963.
5 G. Behr and W. Fliegel, *Sens. Actuators B*, 1995, **26–27**, 33.
6 M. J. Hampden-Smith, T. A. Wark and C. J. Brinker, *Coord. Chem. Rev.*, 1992, **112**, 81.
7 G. Pfaff, *Sens. Actuators B*, 1994, **20**, 43.
8 R. Botter, T. Aste and D. Beruto, *Sens. Actuators B*, 1994, **22**, 27.
9 A. Diegues, A. Romano-Rodrigues, J. R. Morante, U. Weimar, M. Schweizer-Berberich and W. Gopel, *Sens. Actuators B*, 1996, **31**, 1.
10 M. Ando, T. Tsuchida, N. Miura and N. Yamazoe, *J. Chem. Soc. Jpn.*, 1996, **4**, 348.
11 A. A. Vertegel, S. V. Kalinin, N. N. Oleynikov and Yu. D. Tretyakov, *J. Non-Cryst. Solids*, 1995, **181**, 146.
12 A. A. Vertegel, S. V. Kalinin, N. N. Oleynikov and Yu. D. Tretyakov, *Chem. Phys. Lett.*, 1996, **262**, 455.
13 A. A. Vertegel, Dissertation for Candidate of Chemical Sciences Degree, Moscow State University, 1996 (in Russian).
14 I. M. Lifshits and V. V. Slezov, *Zh. Exp. Teor. fiz.* (*J. Exp. Theor. Phys.*), 1958, **35**, 479 (in Russian).
15 I. M. Lifshits and V. V. Slezov, *Fiz. tverdogo Tela* (*Phys. solid state*), 1959, **1**, 1401 (in Russian).
16 C. J. Fonstad and R. H. Rediker, *J. Appl. Phys.*, 1971, **42**, 2911.
17 J. Tamaki, T. Maekawa, N. Miura and N. Yamazoe, *Sens. Actuators B*, 1992, **9**, 197.
18 M. N. Rumyantseva, M. Labeau, J. P. Senateur, G. Delabouglise, M. N. Boulova and A. M. Gaskov, *J. Mater. Sci. Eng. B*, 1996, **41**, 228.

Paper 7/02862H; *Received* 28*th April*, 1997