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1 Introduction

In recent years several papers have reported the synthesis of nanometric titania tubes (TiO_2 , either rutile or anatase) and their applications [1–10]. These nanotubes have been obtained by various methods: e.g., sol-gel synthesis, anodization, electrodeposition, hydrothermal treatment in autoclave. It has been shown that the titania nanotubes, often arranged in arrays to form meso-macroporous sieves, are useful for several technological applications such as gas sensors, photovoltaic applications, catalysis, immobilization of biomolecules, bone-tissue fabrication, and composite reinforcement.

Taking into account the insulating and inert characteristics of rutile, larger dimension tubules could be envisaged to be useable as corrosion resistant micro-pipettes for manipulation of chemicals and biological fluids. So far, in contrast with the large number of papers dealing with titania nanotubes, only few reports deal with larger needles of hollowed titania. V. N. Rozhanskii et al. [11] describes hollowed micrometric needles of rutile obtained by fusion of titania in borax; these needles are not monocrystals but whiskers, i.e. aggregates of crystals oriented along [001]. C.-L. Fan et al. [12] reports polycrystalline titania fibres that were grown by a liquid mix process and sometimes show a “small hole through the center of fiber”. Finally, C. E. Bamberger et al. [13] describes the preparation of hollowed centimetric needle-shaped “crystals” of rutile by using $\text{Na}_2\text{O} + \text{K}_2\text{O} + \text{B}_2\text{O}_3$ as flux, but no proof that the needles are real monocrystals is given.

The present paper reports the conditions to obtain millimetric straw-like monocrystals of rutile by flux growth.

2 Experimental

Straw-like rutile crystals were first obtained by us as side product of runs devoted to the flux growth of Ti-doped forsterite (Mg_2SiO_4) by using finely powdered MoO_3 , V_2O_5 and Li_2CO_3 in the ratio 55.9:9.8:34.3 wt%

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as melting agent [14]. Subsequently, hollowed rutile crystals were on purpose grown using the same mixture as melting agent and a gel of amorphous TiO_2 prepared from TiCl_4 [15] as nutrient; in some runs, amorphous titania was replaced by synthetic anatase and rutile (Table 1).

Table 1 Growth conditions and morphology of the products. (* Flux composition $\text{MoO}_3\text{:V}_2\text{O}_5\text{:Li}_2\text{CO}_3 = 55.9\text{:}9.8\text{:}34.3$ (wt%), & Flux composition $\text{MoO}_3\text{:V}_2\text{O}_5 = 5.1\text{:}14.9$ (wt%), \$ Flux composition $\text{MoO}_3\text{:V}_2\text{O}_5\text{:Li}_2\text{CO}_3 = 41.6\text{:}7.3\text{:}51.1$ (wt%), ^w without canal.)

Run	Nutrient	Flux	Nutrient/flux	Starting cooling T (°C)	Cooling rate(K/h)	Morphology of the products	Max length (mm)	Needle/canal diameter
R1	TiO_2 gel	*	0.100	1250	2.4	Mainly twins	0.5	w
R2	"	*	0.006	1250	1.9	Needle	3	3
R3	"	*	0.006	1350	1.9	Needle	1	4
R4	"	*	0.006	1350	1.8	Needle	2	2.5
R5	"	*	0.015	1250	2.4	Tabular	1	w
R6	"	*	0.006	1250	2.4	Tabular	-	w
R7	"	*	0.006	1350	1.9	Needle	2	4
R8	"	*	0.032	1350	1.6	Needle	2	5
R9	"	*	0.042	1350	1.6	Needle	10	5
R10	"	*	0.100	1350	1.9	Mainly twins	0.8	1.5
R11	"	*	0.015	1350	1.8	Needle	3	1.5
R12	"	*	0.009	1350	1.8	Tabular	3	w
R13	"	*	0.009	1350	1.6	Tabular	2	w
R14	"	*	0.018	1350	1.6	Needle	1	w
R15	Rutile	*	0.015	1350	1.8	Needle	1	3
R16	Anatase	*	0.042	1350	1.6	Mainly aggregate	1	10
R17	Rutile	*	0.006	1250	2.4	Needle	0.3	1
R18	TiO_2 gel	&	0.006	1350	1.6	Aggregate	-	w
R19	"	Li_2CO_3	0.006	1350	1.6	Aggregate	-	w
R20	"	Absent	-	1350	1.6	Aggregate	-	w
R21	"	\$	0.012	1350	1.6	Aggregate	-	w

The products were investigated by: (1) X-ray powder diffraction (XRD; Philips PW 1730 operated with Cu-K α radiation at 40 kV and 20 mA); (2) field emission gun scanning electron microscopy (FEG-SEM; FEI Quanta 200) including compositional information obtained by energy dispersive X-ray spectroscopy (EDS) via an attached EDAX system with Si detector; (3) thermogravimetric and differential scanning calorimetry (TG, DSC; Netzsch STA 449 C Jupiter); (4) microthermometry (Linkam THMSG 600 heating-freezing); (5) μ -Raman spectroscopy (μ RS; Horiba Jobin Yvon HR800); (6) X-ray single-crystal diffraction (four-circle Siemens P4 diffractometer, MoK α radiation).

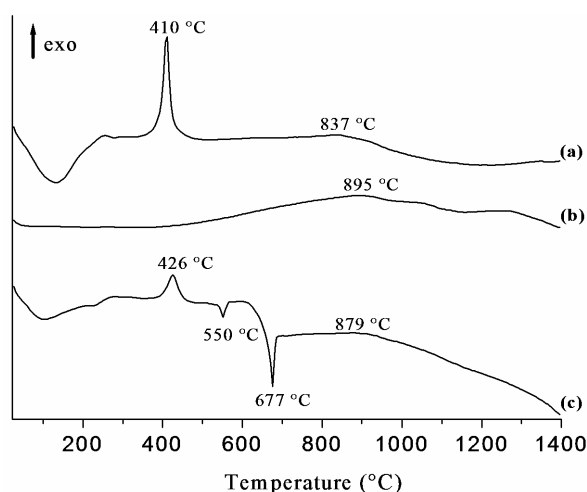


Fig. 1 DSC curves of (a) TiO_2 gel, (b) anatase and (c) gel plus flux.

All chemicals used in the experiments were Carlo Erba products with purity higher than 99%. The starting materials, with different nutrient/flux ratios (Table 1), were mixed in an agate mortar. The mixture was then transferred to a 50 ml platinum crucible and brought, in eight hours, either to 1250°C or 1350°C (Table 1)

within a vertical furnace equipped with Super Kanthal heating elements. The melt such obtained was kept at that temperature for 36 h, then slowly cooled down to 750°C and, finally, rapidly quenched down to room temperature by immersion of the crucible in water. On the whole, the preparation time was about 350 h per run; the cooling rate from 1250 or 1350 to 750°C is reported in table 1. The given temperatures were chosen on the basis of DSC curves (Fig. 1) of Carlo Erba anatase, amorphous TiO_2 gel and the same gel plus flux with composition $\text{MoO}_3\text{:V}_2\text{O}_5\text{:Li}_2\text{CO}_3 = 55.9\text{:}9.8\text{:}34.3$ wt%. As tested by XRD, it turns out that amorphous TiO_2 crystallizes to anatase between 410 and 426°C and anatase transforms to rutile between 837 and 895°C (see exothermic peaks in Fig. 1). These temperatures are in agreement with those given in literature and may change, according to the specific experimental conditions [16]. The two endothermic peaks shown by DSC are attributed to the transformation (melting) of the flux; the occurrence of melt flux at 750°C has been inspected visually during the process of flux growth.

3 Results and discussion

The crystallization products were morphologically inspected by electron (Fig. 2) and optical (Fig. 3) microscopy and identified by XRD and SEM/EDS chemical analysis. All TiO_2 is crystallized as rutile and the original flux is transformed to Li_2MoO_4 (major phase) that forms arrays of thin-walled hexagonal tubes mixed with VO_2 needles (Fig. 2A).

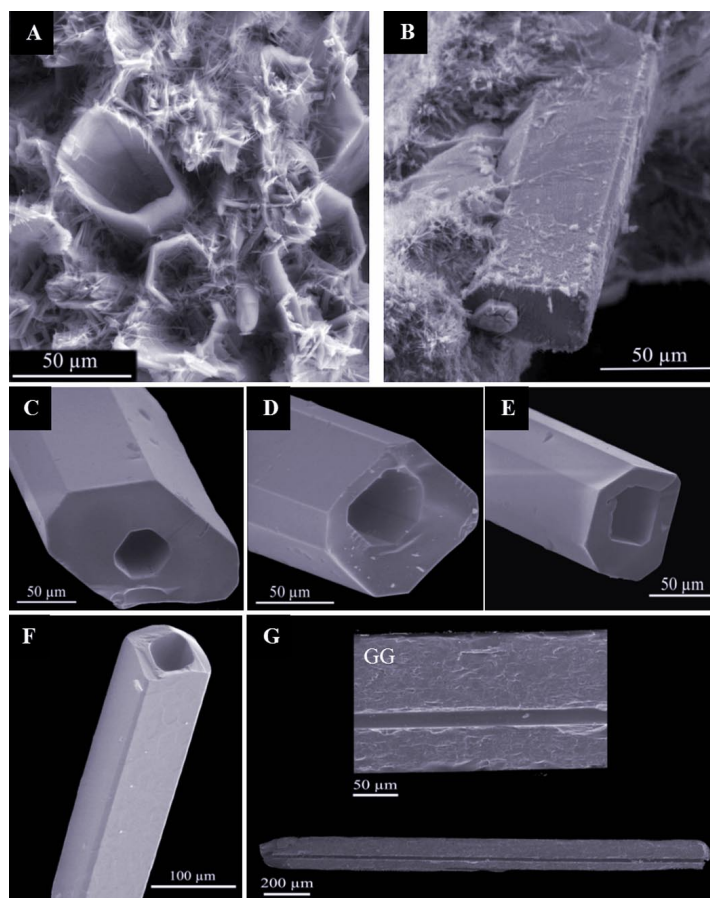


Fig. 2 SEM images of: (A) hexagonal tubes of Li_2MoO_4 and VO_2 needles; (B) rutile needle embedded in and encrusted by solidified flux; (C), (D), (E) and (F) straw-like rutile monocrystals; (G) longitudinal section of a straw-like rutile crystal and enlarged part (GG).

The morphology of Li_2MoO_4 is clearly in agreement with the rhombohedral $R\bar{3}$ crystal structure of this compound [17]. In the majority of the runs, rutile forms needles which, to some extent, are crossed by canals parallel to the [001] elongation direction, as discussed below. The yields of rutile crystals, their morphology and, in particular, the occurrence of canals crossing the full length of the needles depend on the experimental conditions (Table 1). In terms of nutrient, the best results are obtained with TiO_2 gel and the worse ones by

using synthetic anatase. As shown by DSC mentioned above, actually on heating the gel too transforms to anatase, but the morphology of the sharp-edged grains greatly differs from that of the rounded grains of the commercial Carlo Erba anatase. If the nutrient consists of powdered synthetic rutile, only small needles are obtained and very few of them are hollowed. Likely, the gel offers better reactivity because of its morphology and water content. The nutrient/flux ratio and the cooling rate are also crucial: with a ratio higher than 0.1, about 90% of the crystals are twinned and are not hollowed; at cooling rates higher than 2.4 K/h, layered crystals are observed together with hollowed crystals. The average length of the microtubes increases with decreasing the rate of cooling. On the whole, the best yield in terms of straw-like monocrystals of rutile is obtained with a nutrient/flux ratio and a cooling rate in the range 0.015–0.006 and 1.8–1.9 K h⁻¹, respectively. The occurrence of small crystals on the upper internal wall of the crucible suggests that vapour transport could contribute to the crystallization process.

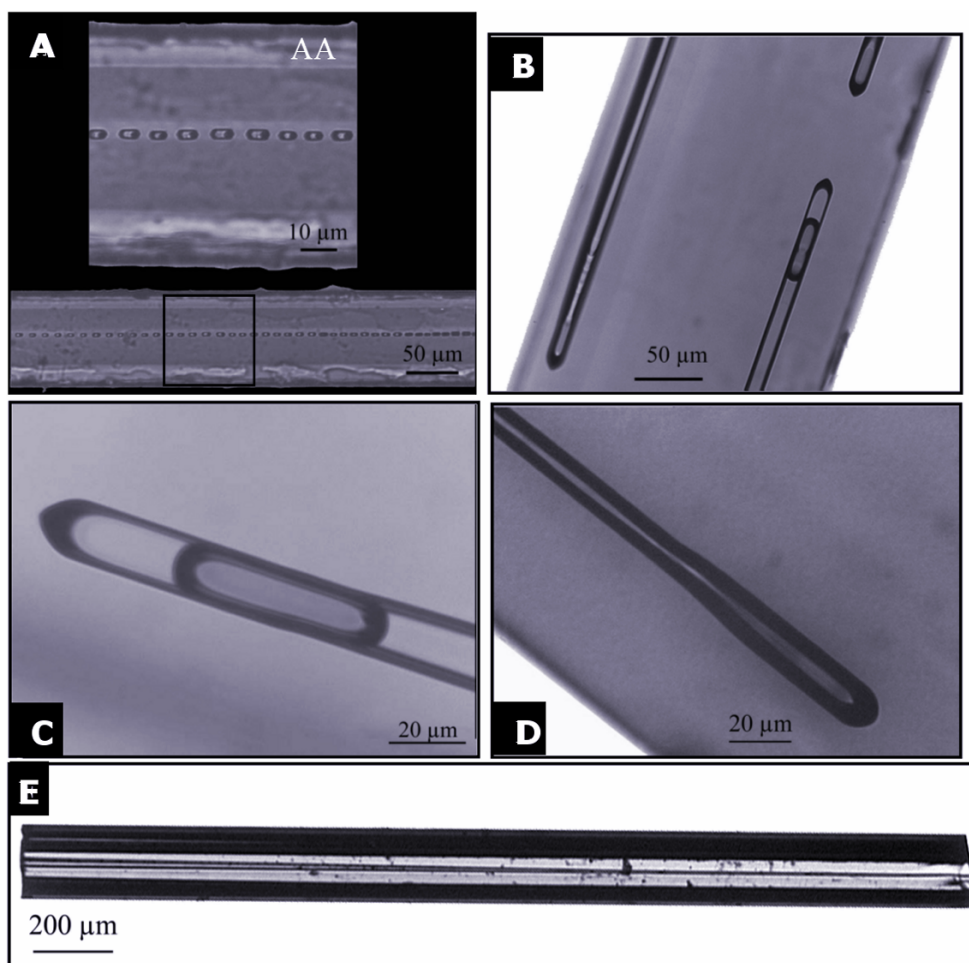


Fig. 3 Optical images: (A) canal containing beads of solidified flux, the enlarged part (AA) shows that each bead contains a bubble (darker part); (B) different canals in the same rutile crystal; (C) enlarged part of (B) to show a bubble (darker) embedded in the solidified flux (lighter) within a canal; (D) the bubble (C) disappears after heating up to 1100°C; (E) canal crossing the full length of a rutile crystal.

The needles of TiO₂ as crystallized appear either embedded in, or encrusted by solidified flux (Fig. 2B) from which they were separated by washing in hot water and finally recovered under an optical microscope; sonication accelerates the washing process. In the straw-like crystals both the inner and the outer surfaces correspond to ditetragonal prisms. Not always the canals cross the full length of a crystal along its [001] directions; sometimes they are interrupted and two or more canals may appear in the same crystal (Fig. 3B). The best straws (i.e., the full-length hollowed crystals) show lengths in the range 0.3–10 mm; the ratio between

the external diameter (range 50–200 μm) and the internal diameter (range 10–70 μm) is in the range 1–10. The straws are stable with increasing temperature as observed by heating up to 1400°C.

The rutile crystals shows a colour from orange to reddish by increasing the nutrient/flux ratio, but are always transparent, thus allowing the exploration of the interior of the hollows both optically (Fig. 3) and by μRS (Fig. 4). It turns out that the canals which do not emerge at one or both tips of the crystals are partially filled by solidified flux which has the same composition as the external solidified flux. Within the canals that do not emerge, the solidified flux contains one or more bubbles; it can even be broken into a row of beads, each consisting of a flux and a bubble part (Fig. 3A). The bubbles do not show Raman bands and likely are empty. They do not evolve under cooling down to -180°C by a stream of liquid nitrogen; instead, under heating the bubbles start to modify at 550°C and, consequently to the melting of the flux, completely disappear at 1100°C (Fig. 3D). At this temperature, actually the melt leaves the canals if these emerge from the crystal. The presence of bubbles suggests that the flux has been incorporated as melt and decreased its volume under solidification. The canals developed along the full length of the rutile needles are empty because of one of the following reasons: the melt could not be trapped; the melt abandoned the canal before solidification; the melt has been removed at the stage of washing and sonication. A combination of the latter two situations is documented in figure 2B where a still encrusted rutile crystal shows a cap of solidified flux which is shaped as the interior of the canals.

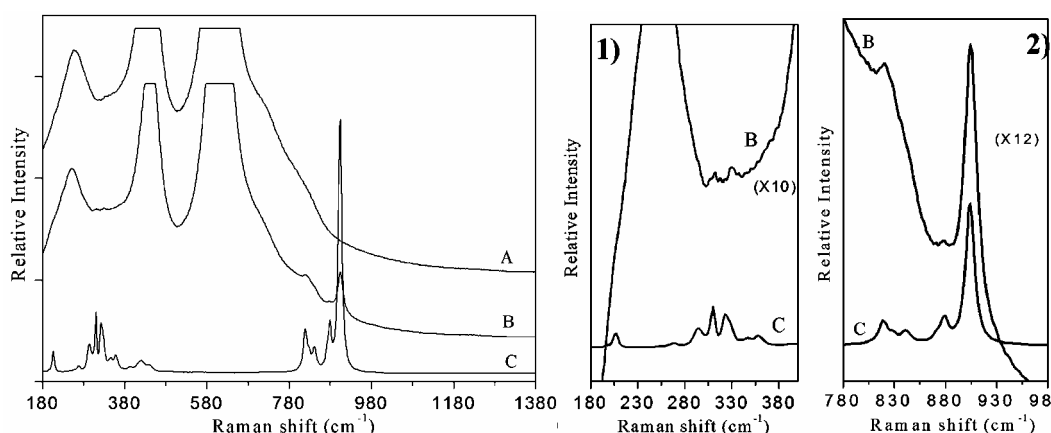


Fig. 4 Raman spectra of: A rutile; B rutile plus flux trapped in its canal; C flux only. 1) zoom in the range 180–400 cm^{-1} of curves B and C; 2) zoom in the range 780–980 cm^{-1} of curves B and C.

4 Conclusions

Straw-like millimetric monocrystals of rutile have been obtained by slowly cooling down to 750°C from 1350°C suitable mixtures of flux (MoO_3 , V_2O_5 , Li_2CO_3) and amorphous TiO_2 gel. As already discussed by [11], it is likely that, as for skeletal crystals, the formation of the axial canals is favoured by a lack of nutrient due to the viscosity of the melt associated to the high growth rate of the needles along [001]. Taking into account that in the same runs also Li_2MoO_4 forms hollowed elongated crystals, the role of the physical properties of the melt looks quite important in determining a uniform flow of nutrient to a crystal that fast grows along one direction. A growing mechanism associated with an axial screw dislocation as supposed by [13] looks unlikely because the large cross section of the canals would require a too large Burgers vector.

The nanotubes of rutile reported in literature and mentioned in the introduction are used mainly as sieves and large free-surface materials. The larger millimetric straw-like monocrystals of rutile we have obtained open the possibility of manufacturing micropipettes of inert rutile for manipulation of chemicals and biological fluids at submillimetric scale.

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