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CRYSTAL GROWTH OF STRONTIUM TITANATE $SrTiO_3$

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$SrTiO_3$ crystals have been prepared by flame-fusion growth and from KF–LiF and K–Li–borate fluxes. The crystals are characterized by EPR, absorption spectra, chemical analyses and γ-rocking curves, and the structural perfection of flame-fusion and flux-grown crystals is compared.

The interest in high-quality crystals of $SrTiO_3$ originates from its second-order phase transition at around 105 K,[1] its photochromic effects, from its ideally cubic perovskite structure at room temperature, and from its conductivity ranging from insulating to metallic depending on doping and degree of reduction.

The main application as synthetic gemstone has led to many attempts of crystal synthesis. However, only two companies[2] succeeded in growing large crystals by the flame-fusion technique. Since important details of their process have not been revealed an independent study on crystal growth by flame-fusion and by flux techniques has been undertaken.

FLAME-FUSION GROWTH OF $SrTiO_3$[3]

A versatile flame-fusion apparatus[4] allowing evaluation and control of all growth parameters was used. The powder was prepared by precipitation of the strontium titanyl oxalate followed by heat treatment and careful sieving of the fraction 40–125 microns. In order to prevent overflow of the molten layer on the growing crystals, the evaporating SrO had to be precisely compensated by a corresponding addition of $SrCO_3$ to the $SrTiO_3$ powder. It was found[3] that the crystal growth rate determines the total evaporation loss of SrO. Figure 1 shows the region of excessive SrO where Sr-rich titanates were found in the overflowed melt, and the region of SrO deficiency where rutile was found in Guinier X-ray powder diagrams of the overflowed melt. Growth of large $SrTiO_3$ crystals is only possible in the narrow range, of a width of about 0.1 wt% SrO, between these two regions at the appropriate growth rate. Crystals up to 15 mm diameter and 30 mm length have been grown using a powder with 3.8 wt% excess of $SrCO_3$ with growth rates of 20 to 26 mm h^{-1}.

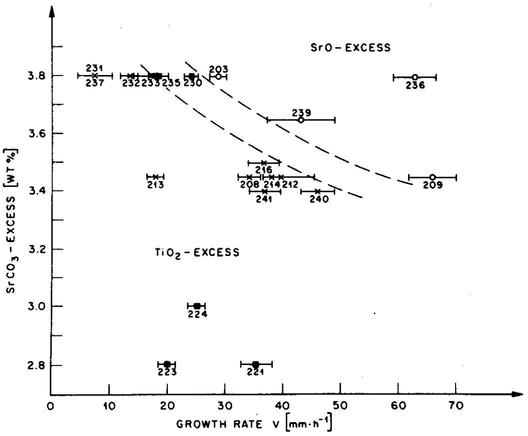

FIGURE 1 Results of X-ray analyses of overflowed melts from experiments with various growth rates and various $SrCO_3$ excess in the $SrTiO_3$ powder. Large $SrTiO_3$ crystals can be grown in the narrow range between the region with SrO excess (○) and the region with TiO_2 excess (x).

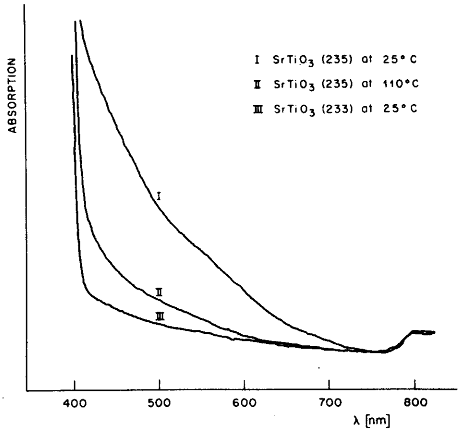

FIGURE 2 Optical absorption of a photochromic brown crystal No. 235 (I), of the same crystal bleached at 110°C (II), and of a nearly colourless crystal No. 233 (III) [$d = 10$ mm].

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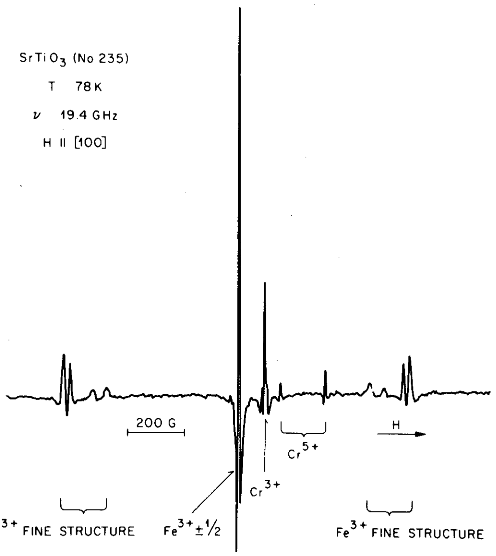

FIGURE 3 EPR spectrum (at 78 K) of the photochromic crystal No. 235.

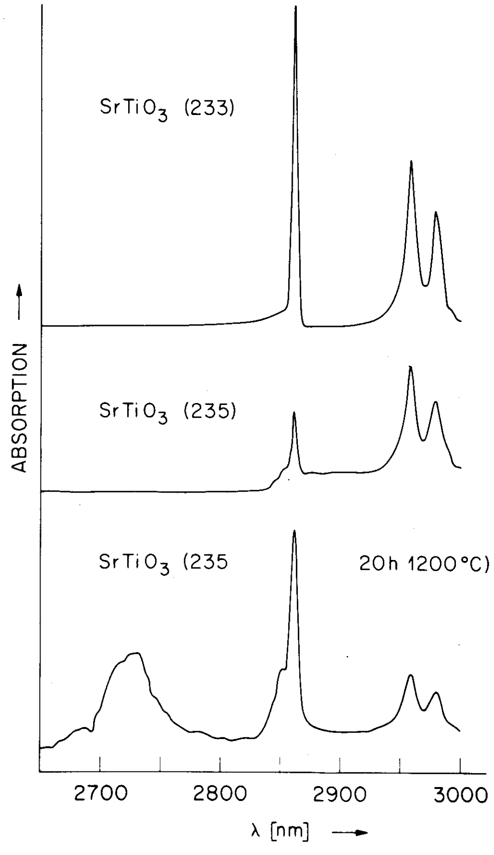

FIGURE 4 Infrared absorption of $SrTiO_3$ No. 233, of the photochromic $SrTiO_3$ No. 235, and of the same crystal after annealing at 1200°C [d = 10 mm].

Crystals prepared from analytical grade starting materials were photochromic: light yellow reversibly changing to brown under the influence of light. By using highly purified starting materials, almost colourless crystals could be obtained. Optical absorption spectra of a photochromic crystal (No. 235) and of a nearly colourless crystal (No. 233) are shown in Figure 2.

EPR of the photochromic crystal (Figure 3) revealed the presence of about 50 ppm Fe and Cr impurities. According to Müller[5] Fe^{3+} replaces Ti^{4+} on an octahedral site, and the compensation of Fe^{3+} by nearby V_0 centres has been described.[6] The photochromic effects of $SrTiO_3$ have been shown to be due to light-induced charge transfer of Fe^{3+} to optically absorbing Fe^{4+} [7] or Fe^{5+}.[8]

The infrared absorption of the colourless and of the photochromic crystals is shown in Figure 4. By annealing the intensity of the two absorption bands at 2960 and 2980 nm (which are not normally found in commercial $SrTiO_3$ crystals) decreased, and simultaneously, the absorption at 2860 nm became stronger. The OH^- concentration was about 10^{17}-$10^{18} \cdot cm^{-3}$.

FLUX GROWTH OF $SrTiO_3$

Attempts to grow $SrTiO_3$ from various fluxes[9] resulted in generally small crystals, only Belruss *et al.*[10] grew large crystals by top-seeded solution growth from excess TiO_2 as solvent.

By using a KF-LiF flux inclusion-free crystal cubes up to 8 mm could be grown. In a typical experiment 108 g $SrCO_3$, 58 g TiO_2, 260 g LiF and 560 g KF were heated in a sealed 600 cm^3 Pt crucible to 1280°. After reducing the number of nuclei by temperature cycling[11] the furnace temperature was lowered from 1250°C linearly by $0.3° \cdot h^{-1}$ to 950°C when the solution was decanted. The EPR lines of Fe^{3+} of the brown crystals were broadened, probably due to fluorine impurities from the solvent. Chemical analyses of various inclusion-free crystals showed 0.33 to 0.62% K, 0.03 to 0.07% Li and 0.15 to 0.22% F.

In order to prevent the detrimental effect of the incorporated fluoride ions, a fluorine-free solvent was searched. Sr-Li-borates gave the best results. In a typical experiment the spectrographic-quality chemicals (Johnson-Matthey) 539 g $SrCO_3$, 71 g TiO_2, 70 g B_2O_3 and 240 g $LiBO_2$ (JMC Spectroflux 100A) were heated in a sealed 500 cm^3 Pt crucible to 1400°C. After temperature cycling, the furnace temperature was decreased from 1350°C by $0.2 \cdot h^{-1}$ to 1050°C when the viscous melt was decanted. The light brown cube-shaped crystals up to a size of 12 x 11 x 9 mm still contain inclusions. It is intended to apply the accelerated crucible rotation technique[12] in order to produce larger and inclusion-free crystals. Chemical analysis showed 0.001% Li in inclusion-free crystals.

STRUCTURAL PERFECTION OF FLAME-FUSION-GROWN AND FLUX-GROWN $SrTiO_3$

Inclusion-free regions of crystals grown from borate flux are isotropic between crossed polarizers, whereas all crystals produced so far by flame-fusion growth and from fluoride flux showed strain birefringence. γ-ray rocking curves obtained from these isotropic $SrTiO_3$ crystals by F. Mezei/Grenoble are shown in Figure 5. The main reflections (020), or (002), are unresolved sharp with a linewidth of less than one minute and with only traces of mosaic. In Table I the dislocation density, the mosaic linewidth of rocking curves and the birefringence are listed for crystals grown by the flame-fusion technique, by top-seeded solution growth (TSSG) and from Sr–Li borate flux. The structural perfection increases in this sequence. These results indicate that the structural perfection is higher the lower the growth rate and the flatter the temperature gradient during crystal growth.

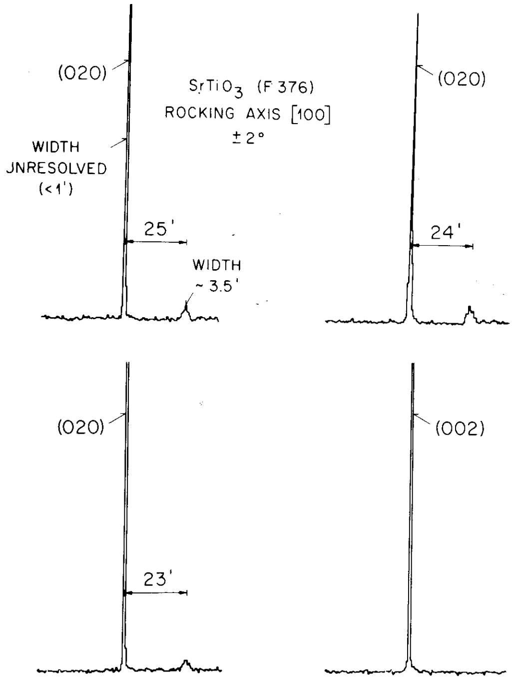

FIGURE 5 γ-ray rocking curves of a $SrTiO_3$ crystal grown from Sr–Li-borate flux.

TABLE I

Comparison of the structural perfection of $SrTiO_3$ crystals grown by various techniques.

	Dislocations/ etch pits per cm^2	Mosaic linewidth of γ- or n-rocking curves	Polarized light
Verneuil	10^6–10^7	5–8′	Much strain
TSSG	10^1–10^2	2–3′	Strain
Sr–Li-borate flux	0–10^2	<1′ (unresolved)	Isotropic

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