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## Crystal growth and characterization of $\text{Ce}_{1-x}\text{Pr}_x\text{O}_2$ ( $x$ similar, equals 0.05) single crystals

Jean-Pierre Chaminade, Roger Olazcuaga, Ghislaine Le Polles, Gilles Le Flem, Paul Hagenmuller

► **To cite this version:**

Jean-Pierre Chaminade, Roger Olazcuaga, Ghislaine Le Polles, Gilles Le Flem, Paul Hagenmuller. Crystal growth and characterization of  $\text{Ce}_{1-x}\text{Pr}_x\text{O}_2$  ( $x$  similar, equals 0.05) single crystals. *Journal of Crystal Growth*, 1988, 87 (4), pp.463-465. 10.1016/0022-0248(88)90094-2 . hal-00262090

**HAL Id: hal-00262090**

**<https://hal.science/hal-00262090>**

Submitted on 19 Mar 2008

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J.P. CHAMINADE, R. OLAZCUAGA, G. LE POLLES, G. LE FLEM and P. HAGENMULLER

### 1. Introduction

The development of rare earth based red pigments with high temperature stability is of great importance for the ceramic industry. Stabilization of praseodymium(IV) in the refractory oxide  $CeO_2$  with fluorite-type structure leads to cerium-rich solid solutions  $Ce_{1-x}Pr_xO_2$  with a strong red color. Crystallographic and optical properties of the sintered powders have been investigated by some of us [1–3]. To explain the origin of the color, we have grown single crystals of a  $Ce_{0.95}Pr_{0.05}O_2$  composition giving as a matter of fact the most attractive red color [2]. A flux growth procedure has been selected, as it appeared previously to be a

convenient technique for growing pure  $CeO_2$  single crystals [4,5].

### 2. Crystal growth

The starting materials used were  $CeO_2$  and  $Pr_6O_{11}$  (from Rhône-Poulenc, 99.99%),  $PbO$ ,  $PbF_2$ ,  $(NH_4)_2HPO_4$ ,  $NaF$  and  $Na_2B_4O_7$  (from Merck, 99.9%).

The powdered  $Ce_{0.95}Pr_{0.05}O_2$  solid solution had been previously synthesized as described elsewhere [2]. The furnace used in this work was a Pyrox "VG70" with lanthanum chromite heating elements, controlled by a Eurotherm "820" regulator and programmer. The mixture (total amount 40–45

Table 1  
Growth conditions for  $Ce_{0.95}Pr_{0.05}O_2$  single crystals

	wt%	Thermal cycle	Results
$Ce_{0.95}Pr_{0.05}O_2$	10	Heating up to 1300 °C at 60 °C/h, 3 h soaking, then cooling down to 900 °C at 1 °C/h, final cooling to room temperature at 100 °C/h	Red transparent cubes with (100) faces up to 3 mm edge and red transparent platelets grown on surface with (100) principal faces of 4 × 2 × 0.5 mm size (fig. 1)
Flux	90		
93.8 wt% $PbF_2$ 3.4 wt% $Pb_3P_2O_8$ 2.8 wt% $NaF$			
$Ce_{0.95}Pr_{0.05}O_2$	10	Heating up to 1200 °C at 60 °C/h, 3 h soaking, then cooling down to 850 °C at 1 °C/h, final cooling to room temperature at 100 °C/h	Red transparent octahedra with (111) triangular faces of 3 mm edge (fig. 2)
Flux	90		
80 wt% $Na_2B_4O_7$ 20 wt% $NaF$			

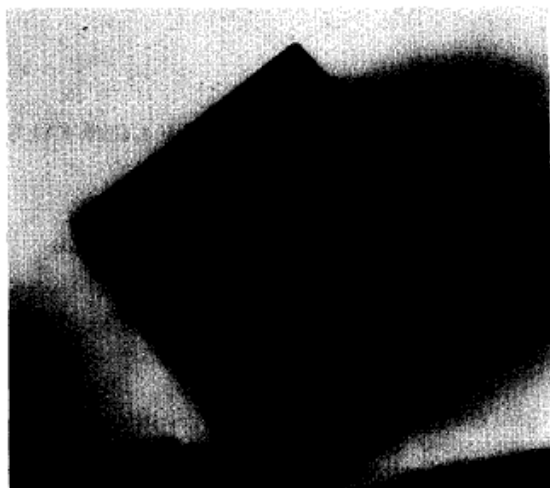


Fig. 1. Red cubic crystal with  $\text{Ce}_{0.95}\text{Pr}_{0.05}\text{O}_2$  formula.

g) of flux and intimately ground  $\text{Ce}_{0.95}\text{Pr}_{0.05}\text{O}_2$  was introduced into a platinum crucible ( $\approx 30 \text{ cm}^3$ ). Once the crucible with a closely fitting lid was put into the furnace, the thermal program was initiated. Starting compositions, thermal cycle and results for two typical runs are collected in table 1.

In every case the crystals were removed by dissolution of the flux in hot diluted nitric acid.

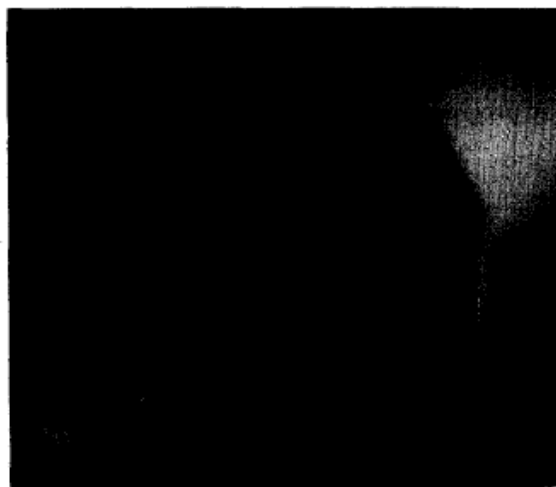


Fig. 2. Hopper on the (111) face of a floating crystal.

### 3. Characterization

#### 3.1. X-Ray diffraction

The crystals obtained were identified by X-ray diffraction. The lattice parameters of the crystals were carefully determined from X-ray powder diffraction data with a Si internal standard and by using a least squares method. The spectra, with in both experiments a lattice constant  $a = 5.410 \pm 0.001 \text{ \AA}$ , are in good agreement with a fluorite-type structure and with those obtained for the cerium rich solid solutions  $\text{Ce}_{1-x}\text{Pr}_x\text{O}_2$  (for  $x \approx 0.05$ :  $a = 5.409 \pm 0.001 \text{ \AA}$ ). Laue photographs (figs. 3 and 4) of the square and triangular faces of the crystals clearly showed four-fold and three-fold symmetry axes characterizing (100) and (111) planes of a cubic fluorite-type related structure.

#### 3.2. Chemical analysis

A lead content of up to 1 wt% was determined by electron probe microscope analysis (EPMA)

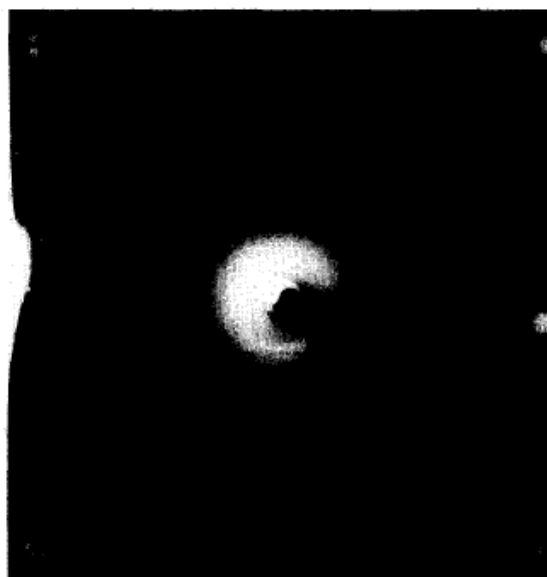


Fig. 3. Laue diffraction pattern on a square face of  $\text{Ce}_{0.95}\text{Pr}_{0.05}\text{O}_2$  crystals.

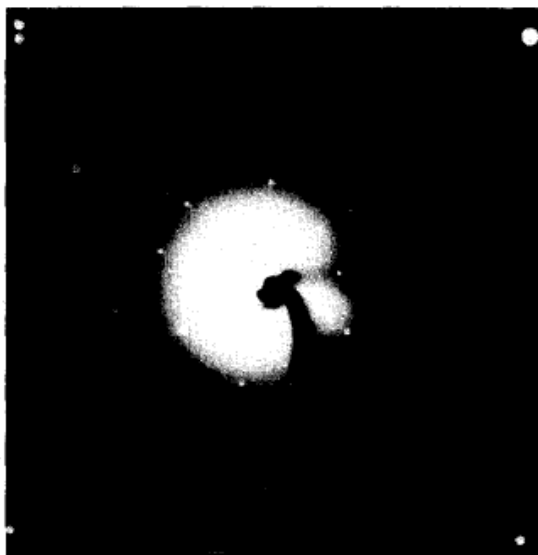


Fig. 4. Laue diffraction pattern on a triangular face of  $\text{Ce}_{0.95}\text{Pr}_{0.05}\text{O}_2$  crystal.

and atomic absorption analysis on crystals obtained from the lead flux ( $\text{PbO}$ ,  $\text{Pb}_3\text{P}_2\text{O}_8$ ).

On the other hand, several crystals grown in the borate flux were analyzed by electron microprobe (Camebax) and compared with the standards  $\text{CeO}_2$  and  $\text{Pr}_6\text{O}_{11}$ . The results gave a composition close to  $\text{Ce}_{0.95 \pm 0.01}\text{Pr}_{0.05 \pm 0.01}\text{O}_2$  and confirmed that the observed red color resulted from the dissolution of  $\text{PrO}_2$  in  $\text{CeO}_2$ . No trace of  $\text{Pr}^{3+}$  has been detected in the crystals either by ESR measurements at liquid helium temperature or by diffuse reflectance spectroscopy at room temperature in the range 400–1500 nm.

Moreover the absorption spectrum of the crystals shows a sharp edge at 640 nm corresponding to an optical energy gap of 1.94 eV (fig. 5). This spectrum can be accounted for by electron transfer from the valence band which has mainly an oxygen p-character to the  $4f^1$  level of  $\text{Pr}^{4+}$  cation according to the model calculated by Koelling et al. for  $\text{CeO}_2$  and  $\text{PrO}_2$  (forbidden bandwidth  $E_g = 6$  eV) [6]. As a consequence the color mechanism can be considered as being in good agreement with the theory of Jørgensen and Rittershaus [7].

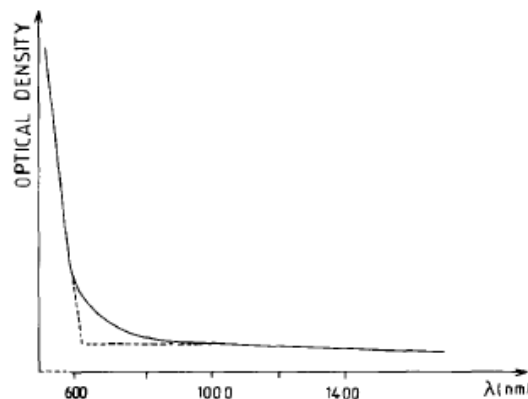


Fig. 5. Absorption spectrum for  $\text{Ce}_{0.95}\text{Pr}_{0.05}\text{O}_2$  single crystal.

As shown in table 1, two growth morphologies were found to exist which depend on two related parameters:

- Temperature: increasing temperature favors the cubic shape.
- Flux composition: flux with acidic character leads to octahedral single crystals ( $\text{Na}_2\text{B}_4\text{O}_7$ ;  $\text{Na/B} < 1$  in this work and  $\text{Li}_2\text{W}_2\text{O}_7$ ;  $\text{Li/w} < 1$  [8]). Flux with basic character leads to cubic shape ( $\text{PbF}_2$ ).

However, an increase of the maximum temperature when borate flux is used results in the occurrence of (100) faces on the octahedra.

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