Mechanical Strength and Thermal Expansion of Sintered Rare Earth Orthophosphate$(RPO)_4$

Yasuo HIKICHI,* Ken-iti HUKUO, and Jiro SHIOKAWA†

Materials Research Laboratory, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466

†*Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamadakami, Suita 565*

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Synopsis. RPO_4 powders, obtained by heating a hexagonal form $RPO_4 \cdot 0.5H_2O$ (R=La, Ce, Pr, Nd, or Sm) or a monoclinic form $RPO_4 \cdot 2H_2O$ (R=Y, Er, or Yb) at 800 °C for 3 h, were pressed into plates or spheres at 500 kgf/cm² (1kgf/cm²=98.0665 kPa) and sintered at 1500 °C for 60 min in the air, the sintered bulk density being above 90% of the theoretical. The mechanical strength and thermal expansion of the sintered RPO_4 are : compressive strength 2300—3000 kgf/cm², bending strength 320—500 kgf/cm², and linear thermal expansion coefficients (30—900 °C) $(5.75—10)\times10^{-6}$.

In a previous paper,[1] a report was given on the freezing point of RPO_4 (R=La, Ce, Pr, Nd, Sm, Y, or Yb) measured by the specular reflection method with a heliostat type solar furnace. However, the mechanical strength and thermal expansion were not reported. The present study reports the compressive strength, bending strength and linear thermal expansion coefficients of RPO_4 sintered at 1500 °C in the air.

Experimental and Results

Starting Materials. Starting materials were powders of a monoclinic form RPO_4 (R=La, Ce, Pr, Nd, or Sm) and a tetragonal form RPO_4 (R=Y, Er, or Yb) prepared by heating a hexagonal form $RPO_4 \cdot 0.5H_2O$ (R=La, Ce, Pr, Nd, or Sm) or a monoclinic form $RPO_4 \cdot 2H_2O$ (R=Y, Er, or Yb) at 800 °C for 3 h in the air.[2-4] The particle sizes of the starting materials were less than 1 μm, the chemical composition being almost the same as the theoretical formula, RPO_4.

Sintering. No detailed study seems to have been reported on the sintering of RPO_4. Preliminary experiments were carried out in order to clarify the relation between the bulk density of the calcined RPO_4 pellets and the calcining temperature.

About 1 g of the starting material was pressed at room temperature into pellets of 10 mm diam. under the pressure of 500 kgf/cm². The bulk densities of the pellets were 2.49 ($LaPO_4$), 2.54 ($CePO_4$), 2.59 ($PrPO_4$), 2.61 ($NdPO_4$), 2.67 ($SmPO_4$), 1.82 (YPO_4), 2.69 ($ErPO_4$), and 2.74 g/cm³ ($YbPO_4$). The pellets were heated at 500 °C, and then calcined at various temperatures (900—1500 °C) for 60 min in an alumina crucible by using a SiC electric furnace. It was confirmed that the alumina crucible does not react with the pellets at temperature below 1500 °C in the air.

The bulk densities of the pellets calcined at 900 °C were the same as those of the starting pellets. However, the pellets began to shrink at temperature above 950 °C, their bulk densities increasing with rise in calcining temperature (Fig. 1). The theoretical densities are 5.04 ($LaPO_4$), 5.16 ($CePO_4$), 5.26 ($PrPO_4$), 5.40 ($NdPO_4$), 5.69 ($SmPO_4$), 4.26 (YPO_4), 6.12 ($ErPO_4$), and 6.36 g/cm³ ($YbPO_4$). The relative densities ((bulk density/theoretical density)×100%) increased rapidly above 1100 °C, becoming greater than 90% at 1500 °C: $LaPO_4$ 97%, $CePO_4$ 97%, $PrPO_4$ 97%, $NdPO_4$ 96%, $SmPO_4$ 94%, YPO_4 91%, $ErPO_4$ 90%, and $YbPO_4$ 92%. Apparent porosity of the pellets calcined at 1500 °C was below 5%. The results show that the sintering of RPO_4 is nearly completed by calcining at 1500 °C for 60 min in the air.

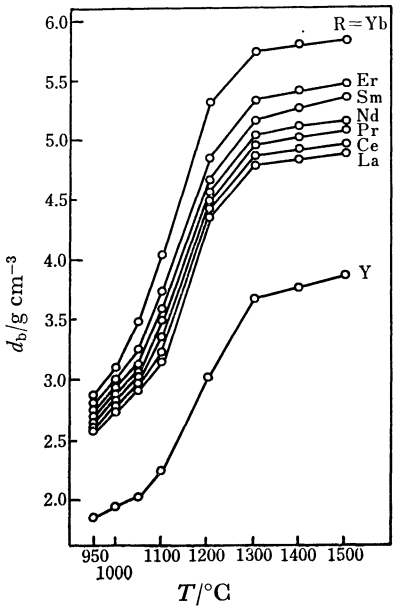

Fig. 1. Relation between the bulk density of the fired RPO_4 pellets and the firing temperature. Firing time: 60 min, d_b: Bulk density.

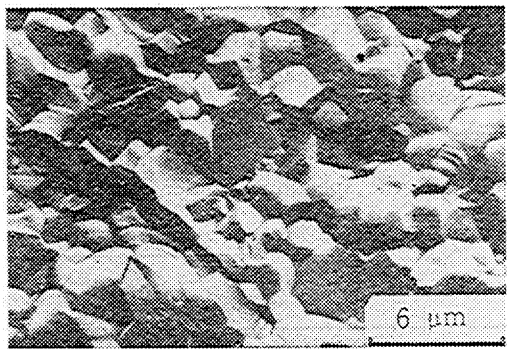

Fig. 2. The fractured surface of the sintered $CePO_4$ at 1400 °C for 60 min, studied by scanning electron microscopy.

Scanning electron micrographs of the fractured surfaces of the sintered pellets show that the structure becomes dense (Fig. 2).

Mechanical Strength. The compressive strength

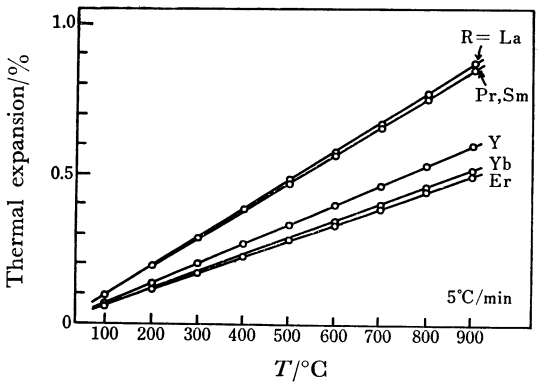

Fig. 3. Thermal expansion curves of the sintered RPO_4.

and 3-point bending strength (gauge length 30 mm) of the specimens sintered at 1500 °C for 60 min were measured. The specimens were cut into the 20 mm × 20 mm × 20 mm size for measurement of the compressive strength, and 50 mm × 20 mm × 10 mm for bending strength. Measurements were carried out for three samples of each sintered RPO_4.

The mean value of the compressive strength for each RPO_4 was in the range 2300—3000 kgf/cm², and that of the bending strength 320—500 kgf/cm². No definite relation has been found between the mechanical strength and the kind of rare earth element.

As compared with some commercial materials, the compressive strength and bending strength of the sintered RPO_4 seem to be larger than those of silica bricks (470—580 kgf/cm² and 27 kgf/cm²)[5] or fire-clay bricks (340—445 kgf/cm² and 57—157 kgf/cm²),[5] and almost the same as those of feldspathic porcelain (1700—3500 kgf/cm² and 100—450 kgf/cm²)[5] or cordierite porcelain (1400—3100 kgf/cm² and 100—200 kgf/cm²)[5] used for insulators.

Thermal Expansion Coefficient. A horizontal dilatometer with a dial gauge (0.001 mm) was used for measurement, the specimen holder and the extension rod being made of silica glass. The specimens sintered at 1500 °C for 60 min were cut into 4 mmϕ × 13 mm in size, and the measurements carried out in the temperature range 30—900 °C in the air with a heating rate about 5 °C/min.

Thermal expansion curves are shown in Fig. 3. The expansion ratio of the sintered $CePO_4$ and $NdPO_4$ at various temperature is close to that of $LaPO_4$, $PrPO_4$, or $SmPO_4$. The linear thermal expansion coefficients of the specimens calculated from these expansion curves are as follows: 10×10^{-6}($LaPO_4$), 9.90×10^{-6}($CePO_4$), 9.66×10^{-6} ($PrPO_4$), 9.77×10^{-6} ($NdPO_4$), 9.66×10^{-6} ($SmPO_4$), 6.90×10^{-6} (YPO_4), 5.75×10^{-6} ($ErPO_4$), and 5.98×10^{-6} ($YbPO_4$).

The thermal expansion coefficients of the sintered monoclinic form RPO_4 were larger than that of sintered Al_2O_3 (30—900 °C, 8.2×10^{-6}),[6] and smaller than that of fused MgO(30—900 °C, 13.9×10^{-6})[6] or fused CaO (30—900 °C, 12.8×10^{-6}),[6] those of the sintered tetragonal form RPO_4 being smaller than that of the sintered Al_2O_3.

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