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Performance of a new furnace for high-resolution synchrotron powder diffraction up to 1900 K, Application to determine electron density distribution of the cubic $CaTiO_3$ perovskite at 1674 K

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Introduction

In situ observation of crystal structures and phase transformations in solid materials heated at high temperatures is of vital importance in many fields such as physics, chemistry, biology, geoscience and materials science. Some research groups measured *in situ* synchrotron radiation powder diffraction (SR-PD) data above 1000 K, however, very less works on precise analysis leading to electron-density distribution above 1000 K. Here we report a new electric furnace to measure the high-resolution ($\delta d/d$=0.03 %) synchrotron powder diffraction profiles from materials at high temperatures up to 1900 K in air.

Design of the new furnace

The authors have designed and fabricated a new electric furnace to measure precisely high-resolution SR-PD data from the specimen at high temperatures up to 1900 K in air (Fig. 1). This furnace is consisted of ceramic refractory with $MoSi_2$ heaters, aluminum body and a sample stage with a spinner and with a controller for the sample-height adjustment. The $MoSi_2$ heaters have some advantages: (1) Maximum temperature can be very high (2100 K for short time and 1900 K for long time), (2) It can be used in air for long periods without degradation, (3) It can make a furnace with a temperature homogeneity compared to a mirror furnace, (4) No low-temperature degradation occurs which often encounters for the $LaCrO_3$ heaters. The specimen can quickly be exchanged without the need for further alignment of the furnace. It should be noted that except for Kapton film for the thermal shield, no part of the furnace is in the paths of the incident X-ray and diffraction signals from the specimen, leading to quality SR-PD data.

Performance of the new furnace

To demonstrate the performance of the new furnace, we measured the diffraction profile of the calcium titanate perovskite at 1674 K and analyzed the data with a combined technique of Rietveld refinement (RIETAN-2000), a maximum-entropy method (MEM, PRIMA) and MEM-based pattern fitting. The refined unit-cell parameter was 3.89846(1) Å at 1674 K. The refined thermal parameters of Ca and Ti atoms (B(Ca)=4.72(4) Å^2 and B(Ti)=1.98(2) Å^2) were smaller than the equivalent isotropic thermal parameter of O atom (B(O)=6.66 Å^2). We have demonstrated that the present system enables accurate structural analysis of calcium titanate perovskite at 1674 K. For the first time the electron density distribution of cubic calcium titanate perovskite is derived in this study (Fig. 2). This electron density indicates the covalent bonding between Ti and O atoms. Comparing with the Ti-O bonds, there existed much less electron density between Ca and O atoms, indicating that the Ca atoms are isolated and more ionic.

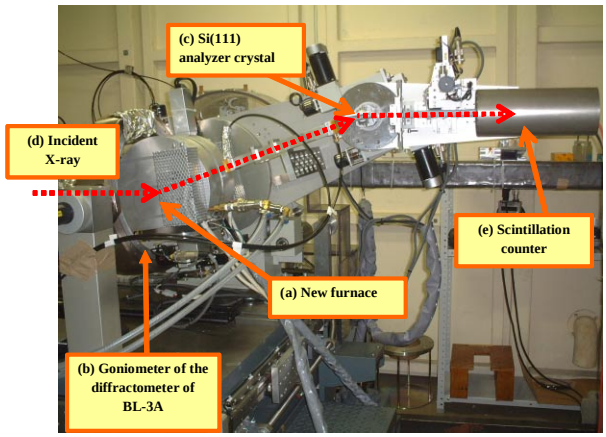

Fig.1. Photograph of the new furnace placed on the stage of the diffractometer at the beam line 3A of the Photon Factory.

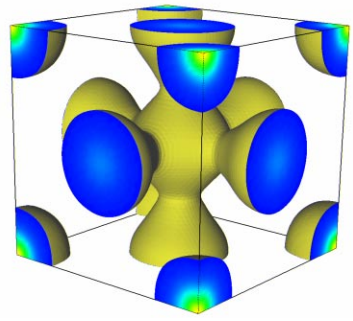

Fig.2. Electron density distribution with equicontour surface at 1.0 e/Å^3 of the cubic $CaTiO_3$ perovskite heated at 1674 K in air. The figure was drawn using a computer program *VENUS* developed by Dilanian and Izumi (2002).

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