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In situ reaction furnace for real-time XRD studies

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The new furnace at the Materials Characterization by X-ray Diffraction beamline at Elettra has been designed for powder diffraction measurements at high temperature (up to 1373 K at the present state). Around the measurement region the geometry of the radiative heating element assures a negligible temperature gradient along the capillary and can accommodate either powder samples in capillary or small flat samples. A double capillary holder allows flow-through of gas in the inner sample capillary while the outer one serves as the reaction chamber. The furnace is coupled to a translating curved imaging-plate detector, allowing the collection of diffraction patterns up to $2\theta \simeq 130^\circ$.

Keywords: X-ray diffraction; *in situ*; temperature control; catalytic characterization.

1. Set-up description

The furnace (see Fig. 1, left) is composed of a main cylindrical vacuum chamber, divided by a water-cooled copper diaphragm (1) acting as thermal barrier, in a hot zone (2) and a cold zone (3). The hot zone houses the heating element (4) while the cold zone hosts the sample alignment stage (5) and gas-flow system (6). The detector system (7) consists of a magnetic and translating curved holder that supports an imaging plate that allows successive X-ray diffraction (XRD) patterns on the same image. The imaging plate is fixed in such a way that a total of 20 cm of film can be exposed with a typical 2θ range of $\sim 130^\circ$. Temperature measurement is accomplished with a thermocouple (8) held at the axis of the heating element near the tip of the capillary.

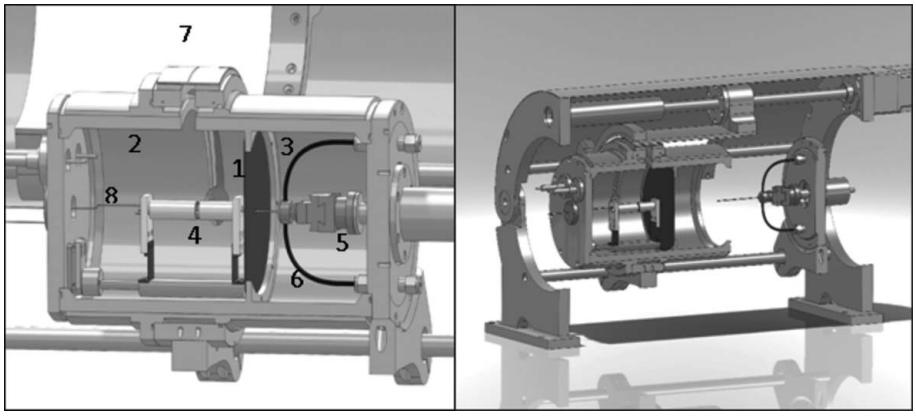

Figure 1
Left: cross-sectional view of the imaging-plate holder and vacuum chamber. The main components of the experimental station are: (1) thermal barrier; (2) hot zone; (3) cold zone; (4) heating element; (5) sample alignment stage; (6) gas-flow system; (7) the detector system which consists of a translating curved holder that supports the imaging plate; (8) thermocouple. Right: cross-sectional view of the open chamber.

The diaphragm dividing the hot and cold zones has a 5 mm aperture at its centre to allow the capillary to extend into the heating element. The capillary base, fixed to the capillary holder in a goniometric head, is inside the cold zone. The entire vacuum chamber slides along tracks perpendicular to the beam path, allowing easy access to the cold zone for replacement and alignment of the capillary (see Fig. 1, right). During measurements the chamber operates under vacuum (10^{-3} bar) in order to avoid air scattering and conductive heat losses.

The structure is located on a wheeled table designed to allow a quick alignment with the beam at the Materials Characterization by X-ray Diffraction (MCX) beamline at the Elettra synchrotron source (Trieste, Italy) (Lausi *et al.*, 2006).

The diffracted beam exits the chamber through an interchangeable Kapton-covered slit (2 mm or 1 mm). The slit is aligned with the ceramic gap of the heating element (see following section) and it extends from $2\theta = -30^\circ$ to 150°. A modified slit integrating a vacuum pipe allows the collection of small-angle X-ray scattering (SAXS) data. The beam stopper, integrated at $2\theta = 0$, prevents the direct beam from hitting the imaging plate but can be easily removed for SAXS experiments.

The hot zone houses the heating element, an alumina tube wrapped in resistive wire. It has an external (internal) diameter of 9.8 mm (8 mm) and a length of 8 cm. The heating wire is made from Kanthal. The ceramic heating element is supported by Macor bars, which are affixed to a removable flange in the chamber. The length of the heating element ensures a negligible temperature gradient (below 2 K cm^{-1} at

1273 K) along the axis of the capillary in the measurement region. Moreover the relative positions of the sample and the heating element are fixed with a reproducibility better than 0.02 mm, and thus any radial temperature gradient is not an issue. The maximum heating rate is 40 K min^{-1} with an accompanying temperature lag below 1 K.

The cold zone houses the capillary holder and the goniometer head used to align the capillary along the axis of the furnace. The holder accommodates capillaries with diameters ranging from 0.1 mm to 2 mm. As an alternative to the capillary a thin-film holder can be mounted on the goniometric head. The capillary holder mounts two concentric capillaries. The gas enters through the sample in the open-ended inner capillary and flows away through the outer capillary, making it possible to control the atmosphere during measurements or to simulate catalytic conditions. A gas analyzer could be used to analyze the exhaust gas composition in real time. During measurements a motor rotates the capillary on its axis ($\pm 90^\circ$) to randomize the orientation of the sample without interrupting gas flow (Chupas *et al.*, 2001, 2008; Clausen *et al.*, 1991; Ermrich *et al.*, 1997; Yashima & Tanaka, 2004).

The furnace and associated infrastructure are supported on a wheeled table, and include two sets of slits, two ionization chambers, the shutter and the motors necessary for beam collimation and alignment. The temperature and gas flow controls, the imaging-plate advance and the shutter mechanisms are computer-controlled through a dedicated software locally developed in *LabView* (National Instruments). The collection geometry was validated by measuring the pattern of the standard sample (NIST Si 640c) at regularly spaced positions along the imaging plate (see Fig. 2).

The relation between the temperature of the sample and that at the thermocouple near the tip of the capillary was determined using a standard platinum powder sample using the relationship between temperature and lattice parameter (Kirby, 1991; Siah *et al.*, 2005; Edwards *et al.*, 1951). The patterns were collected by mixing the Pt powder with carbon black to minimize the absorption of the X-ray by the sample effect. Carbon black's amorphous structure does not add new peaks to the Pt pattern: it is chemically stable and does not react with platinum even at higher temperatures. Moreover, it creates a reducing environment that minimizes oxide formation at high temperatures.

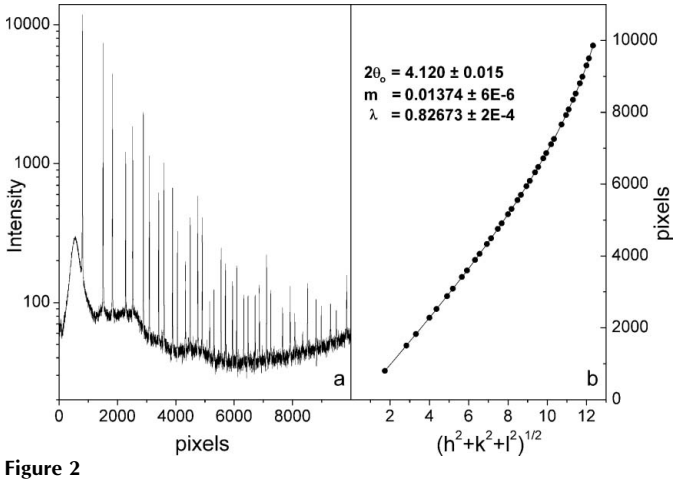

Figure 2
(*a*) Silicon pattern acquired at 15 keV with the natural unit in pixels. The broad peak of the background is due to the silica capillary. (*b*) Fitting of equation $p_{hkl} = (2/m)\,a \sin[\lambda(h^2 + k^2 + l^2)^{1/2}/2a] - (2\theta_0/m)$ to the observed position of the peaks in pixel units p_{hkl}: a linear relation $2\theta_{hkl} = mp_{hkl} + 2\theta_0$, between p_{hkl} and $2\theta_{hkl}$ is assumed. λ (Å), m (° $pixel^{-1}$) and 2θ (°) are the refined parameters. The unit cell of the NIST silicon reference 640c is a = 5.4311946 Å.

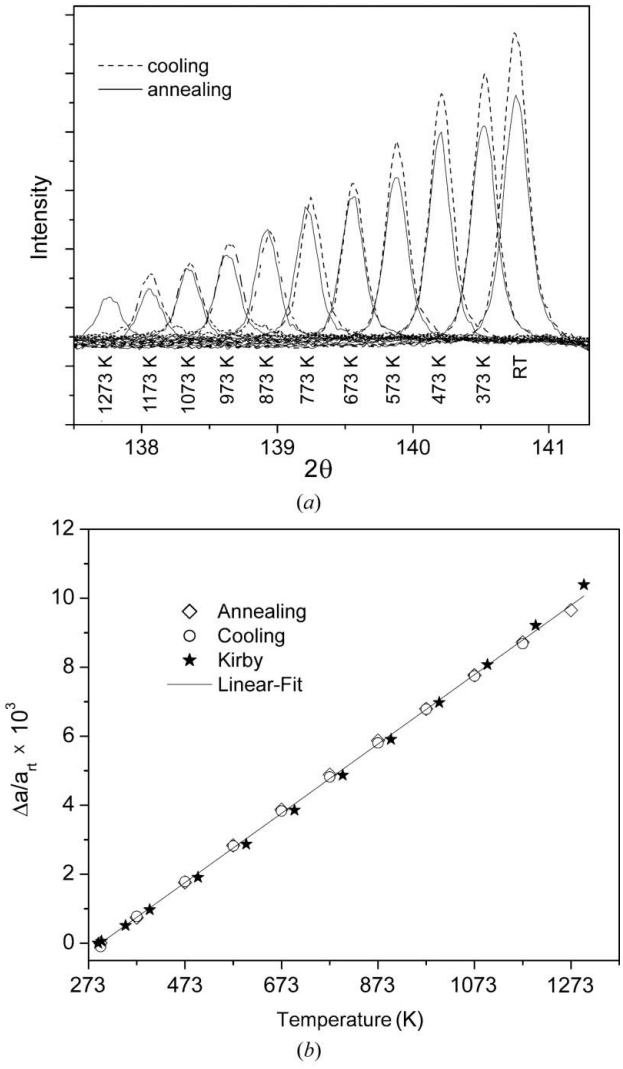

Figure 3
Top: shift of the Pt (533) peak owing to thermal expansion. The solid curve shows the patterns collected during heating; dotted lines are used for the patterns collected during cooling. Bottom: platinum sample. Relative expansion of the lattice parameter. The slope k of the line $\Delta a/a = k(T - T_{rt})$ are, respectively, (1.004 ± 0.004) × 10^{-5} (heating), (1.003 ± 0.004) × 10^{-5} (cooling) and (1.000 ± 0.008) × 10^{-5} (Kirby).

Fig. 3 (bottom) compares the relative variation of the wavelength-independent reticular parameter $\Delta a/a_{rt} = (a_T - a_{rt})/a_{rt}$ obtained from the analysis of the Pt peaks and data presented by Kirby (1991). The two data sets are clearly in agreement, and confirm the calibration and positioning of the thermocouple.

2. Gas-flow test

The gas-flow system was tested using a sample of hematite (pre-annealed to 973 K) and verifying the transition to magnetite in hydrogen-rich atmosphere. In air, this transition does not occur.

The XRD analysis was performed by acquiring 12 discrete diffraction patterns (X-ray energy 12 keV) at increasing temperatures. The transition occurs at approximately 823 K. The transition can be observed in Fig. 4 where some of the extracted patterns are shown. The sample in 4% H_2/N_2 has still the hematite structure at 673 K while it is completely transformed to magnetite at 873 K. At 823 K both the phases are visible.

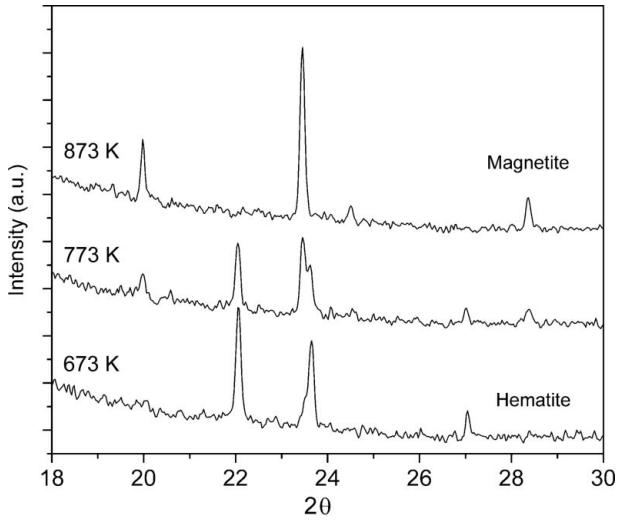

Figure 4
Transformation of hematite (PDF 33664) to magnetite (PDF 19629) in a hydrogen-rich atmosphere. Patterns were acquired at 12 keV.

3. Conclusions

A new furnace has been designed for use at the Materials Characterization by X-ray Diffraction beamline at the Elettra synchrotron source (Trieste, Italy). The apparatus provides an atmosphere- and temperature-controlled environment for powders in capillaries and a temperature-controlled environment for thin-film samples. The sample can be radiatively heated by a furnace up to 1273–1373 K inside a chamber that operates under vacuum (10^{-3} bar) in order to avoid air scattering and conductive heat losses.

The diffraction patterns are collected on a curved imaging plate that can be exposed with a 2θ range of $\sim 130^{\circ}$. The temperature of the oven, the ramp and the data collection conditions are all programmable according to parameters specified by the user.

It is possible to oscillate the sample capillary ($\pm 90^{\circ}$) during the data collection to reduce the effects of preferred orientation.

The wide temperature range and the control of the atmosphere of the furnace provide enough flexibility to perform kinetic studies of solid state chemistry. The possibility of fluxing gases through the powders is fundamental for this kind of analysis and for catalysis especially if we consider that the exhaust gases could be also analysed to study their interaction with the solid state.

The reliability of the oven and of the temperature control has been verified by using the Pt thermal expansion as temperature test while the transformation of hematite (Fe_2O_3) to magnetite (Fe_3O_4) in reducing atmosphere has been used as a test of the atmosphere control.

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