Time-resolved studies of phase transformations using high-temperature powder diffraction

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Introduction

The primary concern with current high-temperature x-ray diffraction (HTXRD) systems is that they employ a flat-plate (Bragg-Brentano) geometry. During peritectic decomposition, the solid fraction, usually denser, can sink below the penetration depth of the x-rays. There are also other errors introduced by this design, including large temperature gradients, sample shift from ideal focus during heating, and inability to rotate the sample to achieve powder averaging. *In situ* study of phase formation requires overcoming these technical hurdles. High-energy x-rays (>20 keV) allow for a transmission geometry (Debye-Scherrer) to be used. This permits a sealed, cylindrical geometry of the sample, preventing liquid/solid separation and incorporating sample rotation [1,2]. In addition, a tube furnace design with low thermal gradients across the sample can be used.

Methods and Materials

The use of an area detector precludes using the analyzer crystal, resulting in a dramatic loss in resolution since the sample cross section is projected directly onto the area detector. The only ways around this are either to use very small samples, which would greatly reduce diffraction, requiring longer counting times, or to place an area detector far back from the sample. A number of image plate configurations were employed in two experimental runs (SRI-CAT, 1-ID) at nominal energies of 47 and 60 keV and distances of 0.7 to 1.3 m from the sample to the plate. A number of geometrical corrections greatly increased the difficulty in analyzing the data (Figure 1). These corrections are primarily rotations which arise from imprecise mounting of the image plate stage, while an additional rotation about normal to the plate comes from feeding the plate into the image reader. Corrections for the other orthogonal rotations are performed using multiple scans of a standard (NIST Si) across the entire plate. The rotation correction is determined by exposing only a 1 mm strip of the plate and shuttering the beam while translating the plate. Furthermore, a higher degree of accuracy could be obtained by placing a Si standard into the beam after the sample to imprint a fiducial mark [3]. Depending on the sample diameter, absorption, and diffraction characteristics, exposure for each strip varied from 3 to 20 seconds.
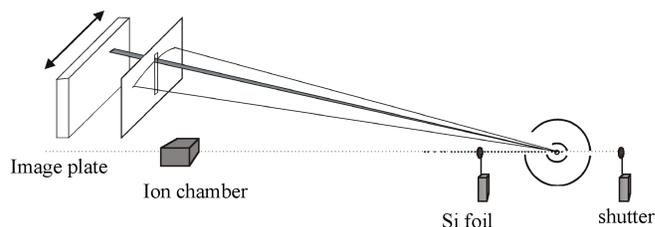

Figure 1: A schematic of the beamline showing the relative position of the furnace to the shutter and image plate.

Results

A number of systems were investigated over the past year, including Fe_3Al, $BaCO_3$, $SrCO_3$, $Bi_2Sr_2CaCu_2O_x$ (Bi-2212), $(Bi,Pb)_2Sr_2Ca_2Cu_3O_y$ (Bi-2223), La-Ni-Sn, and Ti-Zr-Cu-Ni. Some experiments were specifically done to look at order-disorder (Fe_3Al), some to observe solid-state phase transformations (e.g., the carbonates and Ti-Zr-Cu-Ni), and some to observe transient melting (i.e., peritectic reactions). To check the time-resolving capabilities of this new system, a detailed study on a thermal analysis standard, $SrCO_3$, was undertaken. $SrCO_3$ undergoes a first-order solid-state phase transformation from the orthorhombic space group (Pmcn) to the rhombohedral space group (R-3m) at 928° C in 1 bar of O_2. This transformation is used as a thermal analysis calibration standard due to its fast transformation kinetics, which make it an ideal model system for observing nucleation and growth kinetics of a first-order transformation. The high-temperature c-lattice parameter shows reversible behavior on heating and cooling. This demonstrates the lack of significant temperature hysteresis between heating and cooling due to thermal lag of the furnace. Any deviation from reversibility, then, can be reasonably attributed to real sample effects rather than furnace-induced artifacts. This is important since the cell parameters do show hysteretic behavior. The newly nucleated phase seems to be anisotropically strained along the a-lattice direction, and this strain slowly relaxes over time (Figure 2).
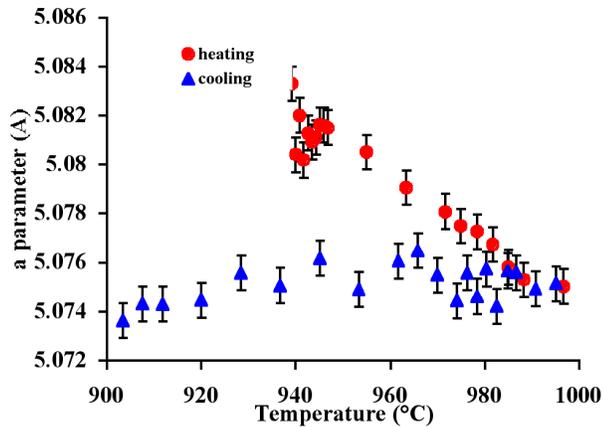
Figure 2: Differences in the rhombohedral a-lattice parameter upon heating and cooling.

Another system investigated in this project was the Bi-2212 ceramic superconductor. A point of contention between quenching studies and conventional high-temperature x-ray diffraction is the existence of the Cu-free $Bi_9(Sr_{1-x}Ca_x)_{16}O_x$ (9115) phase in the high-temperature partial melt. It was suggested that this phase is denser than the liquid and may sink below the penetration depth of the x-rays in conventional systems [4]. Data were collected while heating at 1° C/min in 100% O_2 through the first peritectic reaction at 890° C (Figure 3). Ten second exposures were taken every minute. The peritectic reaction is clearly captured and crystalline peaks in the partial-liquid phase region could be indexed to the $(Sr_{1-x}Ca_x)_{14}Cu_{24}O_{41}$ (14,24) and (9115) phases. This clearly demonstrates that phase segregation does occur during the peritectic reaction in the previous HTXRD experiments.
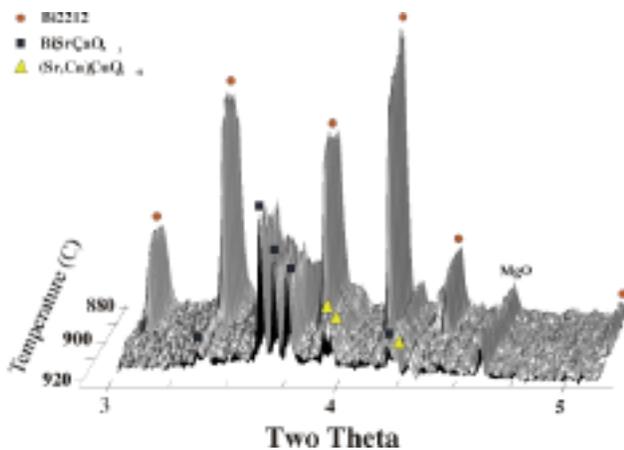

Figure 3: Peritectic decomposition of Bi-2212.

One of the goals of this project is to analyze phase changes in complex materials under real processing conditions. The Bi-2223 powder in-tube process is highly complex. Partially reacted ceramic powder is packed into a Ag tube, which is drawn, rolled and then heat treated with an empirically derived sequence of ramps and soaks. The ceramic undergoes a number of transient liquid reactions at

relatively low temperatures (600° C). In addition, the Ag sheathing is a reactive component in this system. The transmission geometry for this furnace design, the atmospheric control (8% PO_2), and the ability to control the sample rotation allowed us to study the phase changes in an actual tape identical to laboratory processing conditions.

Results from our *in situ* study show that the temperature of crystallization of Bi-2212 during heating changes markedly with the temperature of the intermediate pause in the region of 600° C (Figure 4). During this pause, a calcium-lead phase forms, and the degree of conversion to this calcium-lead phase has a profound effect on the subsequent crystallization of the Bi-2212 phase. At temperatures above 800° C, the calcium-lead phase decomposes and the conversion of Bi-2212 to Bi-2223 begins. The phase content at the reaction temperature changes markedly with the time and temperature of the pauses in the ramp to the reaction temperature. We have demonstrated that by being able to directly follow the reactions *in situ*, the Edisonian approach to materials processing can be eliminated.
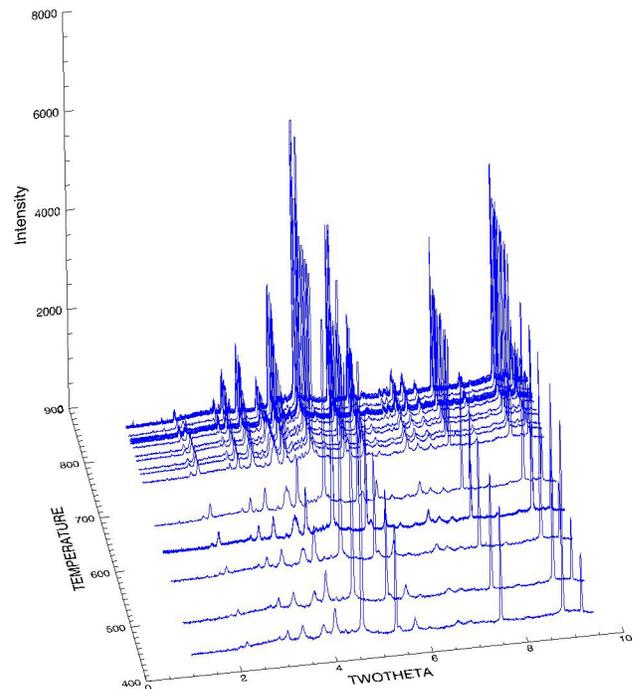

Figure 4: Time-temperature transformations in Bi-2223 tapes.

Discussion

It has been clearly demonstrated that the furnace design provides a highly uniform temperature across the sample. Use of high energies to provide diffraction in transmission allows for time-resolved data to be obtained. This new avenue for materials characterization has a potential for a wide variety of materials. While image plates are not an optimal detector, they do provide sufficient time resolution to see the dynamic effects of phase transformations. Future

work is planned for increasing the time resolution by using a CCD detector.

Acknowledgments

References

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