



Experiment title: In-situ studies of phase transitions and decomposition of Ag₂CO₃ using high resolution Powder diffraction		Experiment number: CH846
Beamline: BM16	Date of experiment: from: 6/2 2000 to: 10/2 2000	Date of report: 23/2 2001
Shifts: 12	Local contact(s): Andy Fitch	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): Poul Norby* , Department of Chemistry, University of Oslo, Norway Robert E. Dinnebier* , Laboratory of Crystallography, University of Bayreuth, Germany		

Report:

Decomposition of silver carbonate, Ag₂CO₃, to metallic silver proceeds via silver oxide, Ag₂O. A reversible thermal transition at ca. 200°C (prior to the decomposition) was observed by Wydeven (1967) using DTA. Ashford and Snelson (1969) observed changes in the powder diffraction patterns of Ag₂CO₃ during heating and cooling. It was later recognized that before the decomposition of silver carbonate to silver oxide, two high temperature modifications of Ag₂CO₃ exist (Van Hattum, JCPDS 31-1236 and 31-1237). The high temperature form has been named α -Ag₂CO₃ whereas the intermediate temperature phase is called β -Ag₂CO₃. However, the crystal structures of the high temperature modifications have not been determined because the intermediate phases decompose rapidly to silver oxide. The decomposition temperature from silver carbonate to silver oxide depends on the partial pressure of carbon dioxide surrounding the sample. Thus, the decomposition temperature can be increased by using a high partial pressure of carbon dioxide. Thereby the decomposition can be suppressed enough to allow powder diffraction data of the high temperature phases to be collected.

In the present experiment we have successfully collected high resolution powder diffraction data powder diffraction data on all phases observed during decomposition of Ag₂CO₃ by using a capillary based micro reaction cell with a carbon dioxide pressure of 4.5 atm. We have determined the crystal structure of α - and β -Ag₂CO₃, and established the thermal expansion properties of the three modifications of silver carbonate.

The sample of Ag₂CO₃ was contained in a 0.7mm quartz glass capillary mounted in a Swagelok fitting (Norby 1997). An internal pressure of carbon dioxide (4.5 atm.) was applied, and the sample was heated using a hot air blower. High resolution powder diffraction data were collected at BM16 using a wavelength of 0.49121(2)Å. A full set of room temperature data was collected. Fast high resolution data were collected during heating. At 203°C phase pure α -Ag₂CO₃ was obtained, and data for structure determination and refinement were collected. The sample was then cooled to 180°C where data on the pure β -Ag₂CO₃ phase were collected. The transformation from β -Ag₂CO₃ back to the low temperature phase is sluggish, and it was possible to obtain unit cell parameters for β -Ag₂CO₃ down to room temperature. The sample was then heated through the decomposition reactions: Ag₂CO₃ → Ag₂O → Ag, allowing the thermal expansion properties to be determined.

The crystal structure of the room temperature and the two high temperature modifications of Ag_2CO_3 were determined using direct methods (EXPO), and refined by Rietveld methods (GSAS):

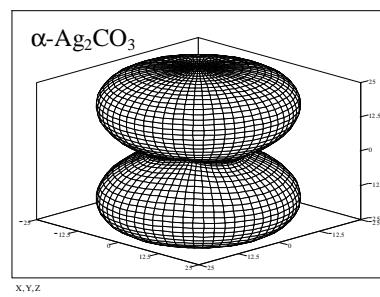
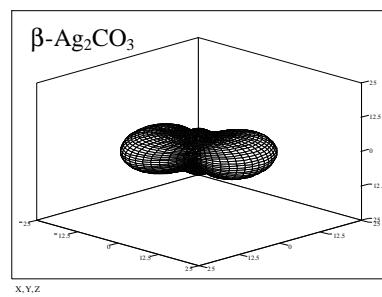
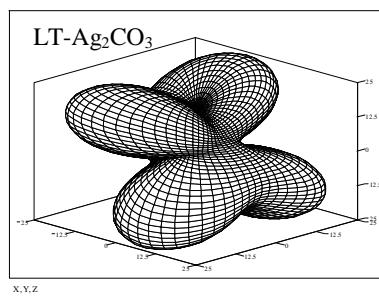
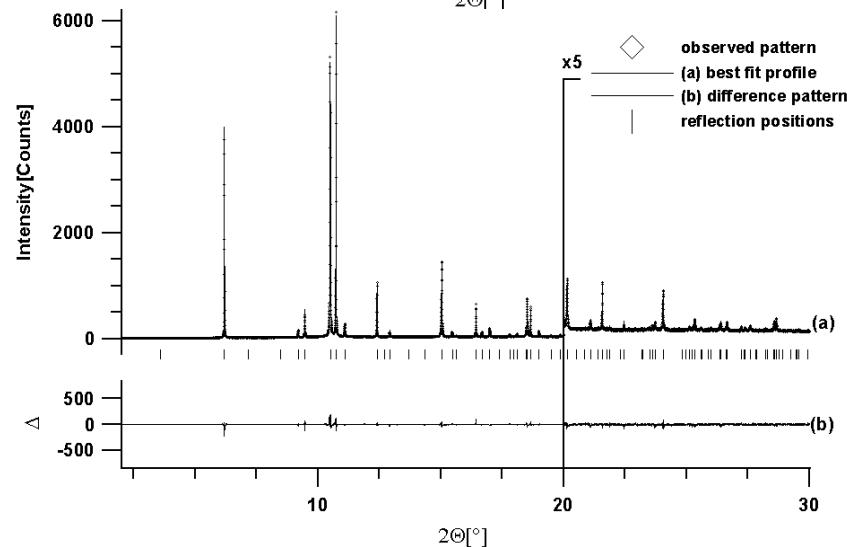
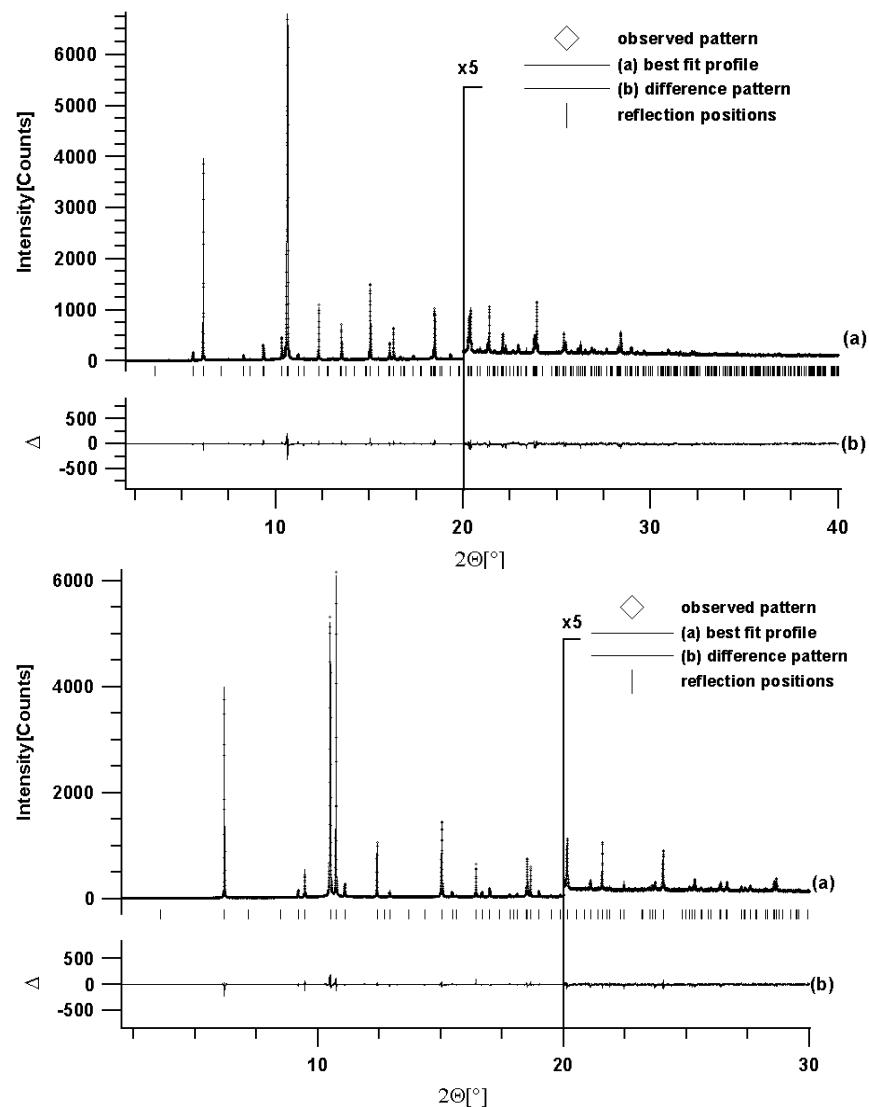
RT- Ag_2CO_3 (25°C): $P2_1/m$,
 $a=4.85209(2)$, $b=9.54888(4)$,
 $c=3.25363(2)\text{\AA}$, $\beta=91.9713(3)^\circ$.
 β - Ag_2CO_3 : (180°C): $P31c$,
 $a=9.17160(4)$, $c=6.51758(4)\text{\AA}$.
 α - Ag_2CO_3 : (203°C): $P\bar{6}2m$,
 $a=9.09243(4)$, $b=3.32494(2)\text{\AA}$

The differences in the crystal structures make it possible to understand the thermal transformation properties. By heating the room temperature phase, a mixture of the two high temperature phases is obtained. By further heating pure α -phase may be obtained, and by subsequent cooling pure β -phase may be isolated. The transformation back to the room temperature phase is very sluggish, and the β -phase may persist until room temperature. The $\alpha \rightarrow \beta$ -phase transition is basically an order/disorder transformation, while the transformation between the room temperature and the high temperature phases involves more extensive atom rearrangement.

The thermal expansion of the three modifications of silver carbonate displays significant anisotropy. A significant abrupt change in the unit cell volume is observed between the low and the high temperature phases, reflecting a significant change in the crystal structure.

The thermal expansion of silver oxide was determined as well. When approaching the decomposition temperature ($\text{Ag}_2\text{O} \rightarrow \text{Ag}$) a decrease in the unit cell volume is observed. Whether this is caused by structural or chemical changes is presently being investigated.

From anisotropic line broadening the internal strain distribution was determined for the three modifications of silver carbonate, displaying significant differences as showed in the Figure below.



Wydeven, T. (1967). *Australian J. Chem.* **20**, 2751.

Ashford, N.A. and Snelson, A. (1969). *J. Chem. Phys.*, **51**, 532-538.

Norby, P. (1997). *J. Appl. Cryst.*, **30**, 21-30