Local structure and dynamics of silver oxide at low temperatures

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Introduction

Diffraction measurements have shown that Cu_2O and Ag_2O are characterized by Negative Thermal Expansion (NTE) over large temperature intervals [1]. Both compounds share the cuprite structure (two interpenetrating lattices, bcc of oxygen atoms, fcc of metal atoms). Besides, diffraction patterns of Ag_2O clearly show a transition to a different phase below 40 K, whose nature has not yet been clarified. EXAFS measurements have been done on Ag_2O up to 500 K, giving original insights on the local origin of NTE [2]. Aim of the present proposal was to complete EXAFS measurements on Ag_2O at low temperatures, to study the phase transition observed by diffraction and to obtain more accurate information about NTE in the cuprite phase (above 50 K).

Experiment

The experiment has been done from 21 to 24 November 2003.

The beam-time allocated to the experiment could not be fully exploited, since a consistent part had to be dedicated to the optimisation of the experimental apparatus and the acquisition software. As a consequence, the original research program (temperature interval 4-200 K, steps of 2 K at the phase transition) could not be fully carried out. EXAFS measurements have been performed on a powdered sample at decreasing temperatures from 90 to 6 K and at increasing temperature from 6 to 50 K. The temperature was controlled by the He cryostat.

The quality of each file, checked in real time through a fast but complete data analysis, was good enough to fulfil the requirements of the project.

Results

The development of a phase transition in the range between 20 and 30 K is directly evident in the EXAFS signal. The Fourier Transform shows a clear modification of the shape of the second shell peak and further modifications in the large distance structures. A preliminary quantitative analysis reveals consistent modifications in both distances and Debye-Waller factors of 1st and 2nd coordination shells. The interpretation of the transition is however still unclear. Work is in progress, in cooperation with G. Artioli (Univ. Milano).

The good quality of spectra allowed a refinement of data analysis above 40 K (cuprite phase). Preliminary results show that the second shell signal (12 Ag) can be reasonably decomposed into the two different contributions of the 6 atoms connected via an oxygen bridge and the other 6 atoms without O bridge; the first distance contracts, while the second distance expands, in agreement with preliminary results obtained for Cu_2O.

Conclusions

The complementarity of EXAFS and diffraction for the study of NTE and phase transitions is confirmed. Data analysis and interpretation is under way to obtain definitive quantitative information.

References

[1] W. Tiano, M. Dapiaggi, and G. Artioli, J. Appl. Cryst. 36, 1461 (2003)

[2] S. a Beccara, G. Dalba, P. Fornasini, R. Grisenti, A. Sanson, and F. Rocca, Phys. Rev. Lett. 89, 025503 (2002).

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