ESRF	**Experiment title:** **Low temperature behaviour of Ag2O**	**Experiment number**: CH-1501
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Names and affiliations of applicants (* indicates experimentalists):

Monica Dapiaggi* Università di Milano

Paolo Fornasini Università di Trento

Mauro Gemmi* Università di Milano

Walter Tiano* Università di Milano

Report:

Silver (I) oxide crystallises in the cuprite-type structure (space group $Pn\bar{3}m$), where metal (M) atoms form a FCC lattice (each M is linearly coordinated to two oxygen atoms), and oxygens form a BCC lattice (each oxygen is tetrahedrally coordinated by four metal atoms) [1]. This structure can also be described as two interpenetrating cristobalite-type lattices. Cuprite (Cu_2O) behaviour with temperature is well studied: there is a number of scientific works on the subject, especially because Cu_2O shows an unusual temperature dependence, being its thermal expansion negative below room temperature, and positive (but very small) over room temperature. More details on cuprite thermal behaviour can be found in [2], [3], [4].

Silver (I) oxide (Ag_2O) is not so widely studied: the only two papers ([5], [6]) about its thermal expansion give a positive thermal expansion coefficient from 100 K to its decomposition temperature (about 500 K). The aim of the work is to measure the thermal expansion of this peculiar structure studying the variation of the lattice constant respect to the temperature. Silver (I) oxide has been studied with much more attention in its local thermal behaviour, by means of EXAFS ([7], and references therein). Silver (I) oxide is a modifier in fast ion conducting glasses (such as AgI-Ag_2O-B_2O_3), and a detailed knowledge of its thermal properties can help understanding the properties of the conducting glasses. The authors showed that the first shell around Ag (i.e. Ag-O bond) is expanding with temperature, while the second shell (Ag-Ag bond) is instead contracting with temperature, but there are clear signs of tetrahedra deformation, so that the negative thermal expansion of this bond cannot be interpreted straightforwardly by means of RUMs. Bond contraction seems to arise, as claimed by the authors, from an average approaching of Ag atoms belonging to different networks, through the empty sites in the intermediate space.

Silver (I) oxide (Figure 1) has a negative thermal expansion all over the investigated temperature range. This result is in disagreement with literature data, reporting Ag_2O thermal expansion as always positive from 100 to 500 K ([5], [6]). The thermal expansion of Ag_2O is always negative in the whole temperature range, although it can be divided into three regions, based on the slope: in the first one the linear thermal expansion coefficient is of one order of magnitude larger than that of cuprite (β=-1.4 10-5 K^{-1}), in the second β=-2.40 10-6 K^{-1} while above room temperature β=-9.02 10-6 K^{-1}.

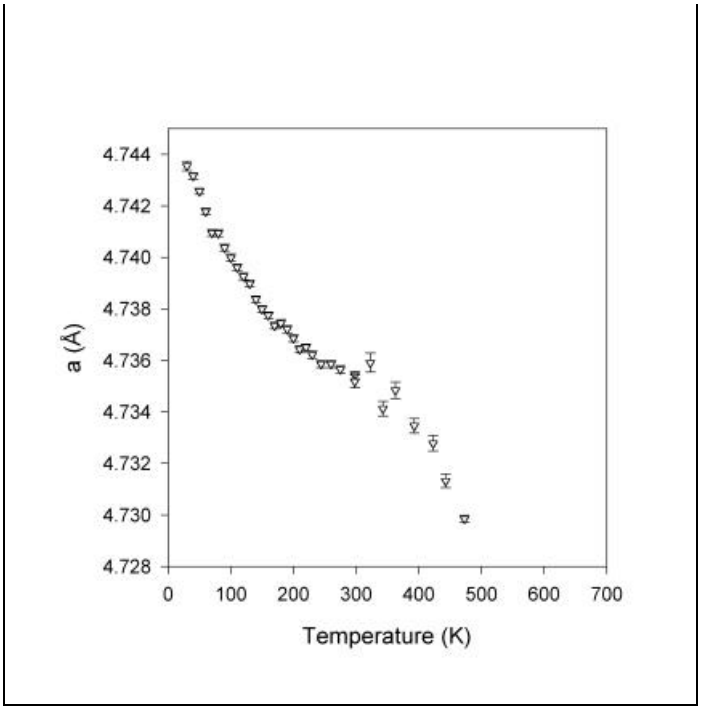

Figure 1 - Thermal expansion of silver (I) oxide

The reported thermal expansion data agree with EXAFS results on Ag_2O, as the second coordination shell (Ag-Ag) shows a negative thermal expansion up to 500 K. A preliminary study on the vibrational behaviour of Ag_2O as a function of temperature [8] showed a significant static disorder on Ag site, evidencing the possibility for the Ag atom to be displaced from its highly symmetric position on the unit cell origin. This is again in agreement with EXAFS data [7], showing a local distortion of Ag_4O tetrahedra. Further studies on the vibrational properties of Ag_2O, in particular for what concerns the comparison of uncorrelated XRD mean square displacements (MSD) with correlated EXAFS MSD are still in progress.

The results on silver (I) oxide thermal expansion have already been accepted by the Journal of Applied Crystallography with the title "Thermal expansion in cuprite-type structures from 10 K to decomposition temperature: Cu_2O and Ag_2O", by Walter Tiano, Monica Dapiaggi and Gilberto Artioli.

References

[1] Wells, A. F., in: Structural Inorganic Chemistry, Clarendon Press, Oxford.

[2] Ivanda, M., Waasmeier, D., Endriss, A., Ihringer, J., Kirfel, A. & Kiefer, W. (1997) Low-temperature anomalies of cuprite observed by Raman spectroscopy and X-ray powder diffraction. J. Raman Spectr. 28, 487-493.

[3] Roy, R., Agrawal, D.K. & McKinstry, H.A. (1989) Very low thermal expansion coefficient materials. Annu. Rev. Mater. Sci. 19, 59-81.

[4] White, G.K. (1978) Thermal expansion of cuprous oxide at low temperature. J. Phys. C: Sol. St. Phys. 11, 2171-2174.

[5] Taylor, D. (1985) Thermal expansion. V. Miscellaneous binary oxides. Br. Ceram. Trans. Journ. 84, 9-14.

[6] Srivastava, S.P., Srivastava, R. C., Pandey, S.D. (1977). Thermal expansion of Ag2O. J. Phys. Soc. Japan, 43, 1463-1464.

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

[8] Tiano, W. (2002) Undergraduate Thesis.