

A difference in thermal behaviour of AgReO_4 and CuReO_4

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Perrhenates of Ag(I) and Cu(I), MReO_4 with $\text{M} = \text{Ag}$ or Cu , have a number of similar physical-chemical properties. They melt congruently at a relatively low temperature, the vapor at high temperature over the compounds consists of MReO_4 , $(\text{MReO}_4)_2$ and Re_2O_7 or MReO_4 , $(\text{MReO}_4)_2$, O_2 and Re_2O_7 molecules, and the enthalpies of formation of $(\text{MReO}_4)_2(\text{g})$ from $\text{MReO}_4(\text{l})$ are nearly the same in the error interval [1,2].

AgReO_4 and CuReO_4 crystallize in tetragonal symmetry, AgReO_4 has a scheelite-type structure (S.G. $I4_1/a$) [3], CuReO_4 represents its own CuReO_4 -structure type ($I4_1cd$) [1]. In both compounds Re-atoms are tetrahedrally coordinated and isolated from each other. Ag atoms occupy dodecahedra connected by edge-sharing. The structure of CuReO_4 represents a three-dimensional framework formed by corner-shared tetrahedra of CuO_4 and ReO_4 . There is a number of large channels between these tetrahedra, which can cause quite different behaviour of thermal expansion in comparison with AgReO_4 .

Low- and high-temperature structure investigations of AgReO_4 and CuReO_4 were performed at beamline B2 [4] in Debye-Scherrer mode using the on-site readable image-plate detector OBI [5], and a closed-cycle cryostat [6] or a STOE furnace. All diffraction patterns have been analyzed by using the software package WinPLOTR [7]. For both structure models, a full-profile Rietveld refinement of all general atomic positions was performed with an isotropic approximation for the thermal displacement parameters, which were refined independently for each kind of cations and for all oxygen atoms together.

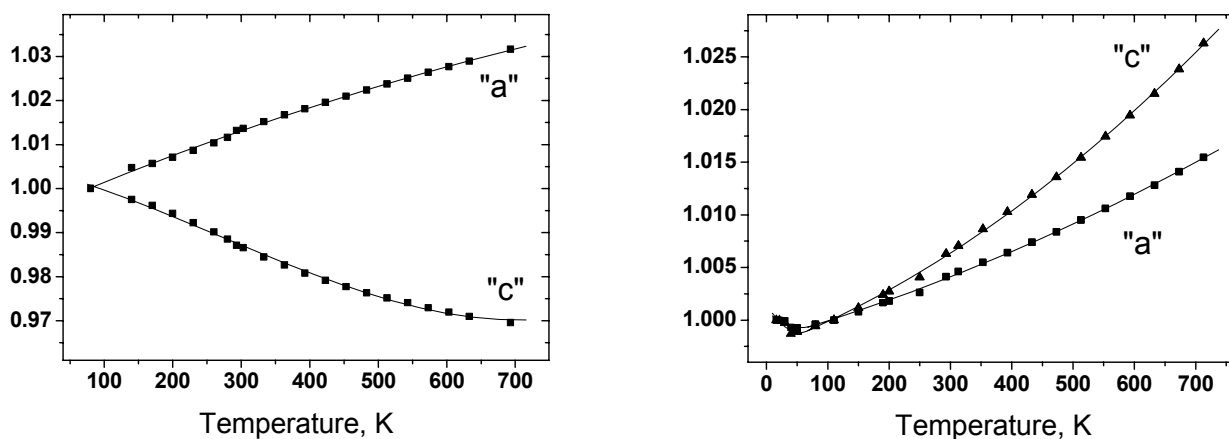


Figure1. Relative change of lattice parameters of CuReO_4 (left) and AgReO_4 (right) vs. temperature.

Whereas a positive thermal expansion along “a”- axis and a negative expansion along “c” – axis was found for CuReO_4 , a positive expansion along “a” and “c” direction was detected for AgReO_4 over the same temperature interval (Fig.1). The increasing temperature leads to a very strong distortion of CuO_4 -tetrahedra around the channels in the structure of CuReO_4 (Fig.2 and 3), but the average distances Cu-O and Re-O do not change significantly. ReO_4 -tetrahedra do not undergo such a distortion. The change of angles (Cu-O-Re), increasing of O1-O2- and decreasing of the O2-O3 - interatomic distances in these CuO_4 -tetrahedra is responsible for the positive expansion in the “a” and “b” and the negative one in “c” direction. In the AgReO_4 structure the positive thermal

expansion in three crystallographic directions is due to increasing average Ag-O –distances in the AgO_8 -polyhedra (Fig.2), whereas the average Re-O distance remains also nearly constant .

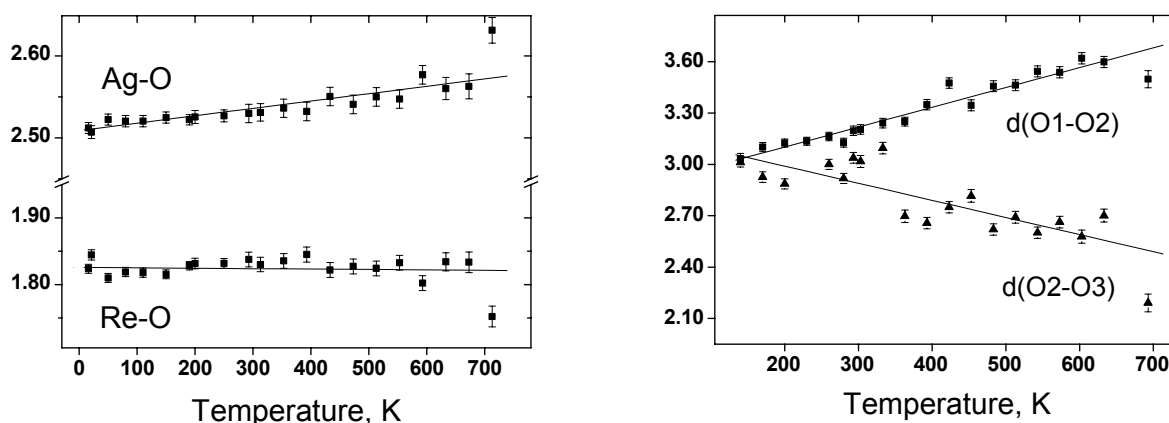


Figure 2. Average interatomic distances (in Å) in AgReO_4 (left) and selected O-O-distances in CuO_4 -tetrahedra, forming the channels in the CuReO_4 structure (right) vs. temperature.

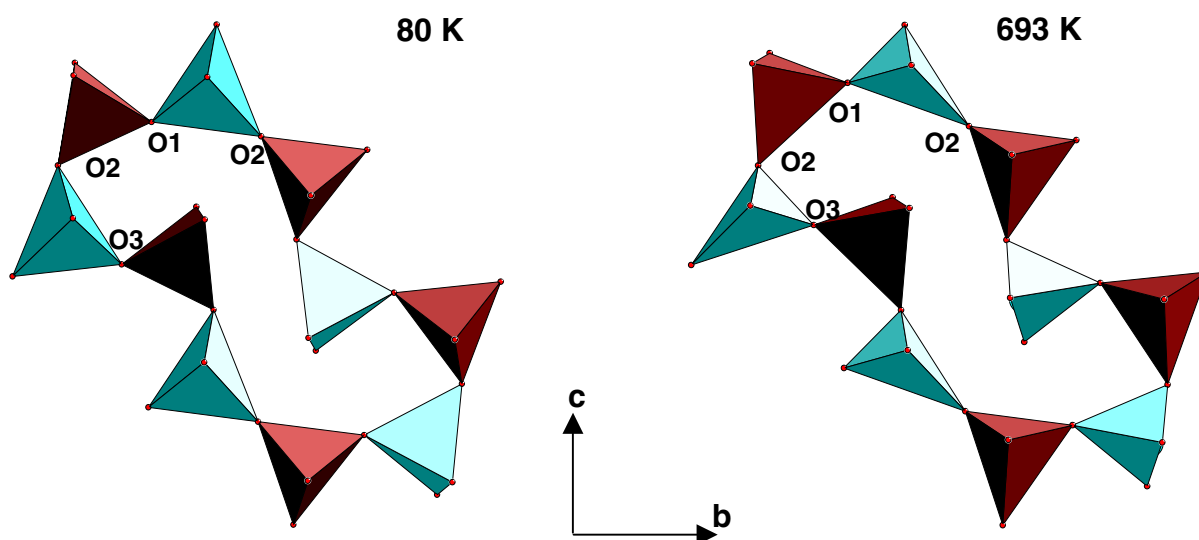


Figure 3. 10-membered-rings in the framework of MO_4 -tetrahedra (CuO_4 – blue, ReO_4 – brown) in CuReO_4 at 80 and 693 K, respectively.

This work is financially supported by DFG (FU125/42).

References

- [1] D. Mikhailova, H. Ehrenberg, H. Fuess, J. Solid State Chem., 179 (2006) 2004-2011.
- [2] Ye. K. Kazenas, Vaporization thermodynamics of double oxides, Moscow: Nauka, 2004, 551 s (in Russ.).
- [3] D. Yu. Naumov, A. V. Virovets, S. V. Korenev, A. I. Gubanov, Acta Crystallogr. C55 (1999) 8.
- [4] M. Knapp, C. Baehtz, H. Ehrenberg, H. Fuess, J. Synchrotron Rad. 11 (2004) 328-334.
- [5] M. Knapp, V. Joco, C. Baehtz, H. H. Brecht, A. Berghaeuser, H. Ehrenberg, H. von Seggern, H. Fuess, Nucl. Instrum. Meth. A 521 (2004) 565-570.
- [6] J. Ihringer, A. Koester, J. Appl. Cryst. 26 (1993) 135-137.
- [7] T. Roisnel, J. Rodriguez-Carvajal, Mater. Sci. Forum 378-381 (2001) 118-123.