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Synthesis and structure determination of copper perrhenate, $CuReO_4$

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Abstract

Copper(I) perrhenate, $CuReO_4$, has been synthesized as a single-phase sample in sealed silica tubes at 500–800 °C, and its structure was determined for the first time by single-crystal X-ray diffraction. $CuReO_4$ forms a new structure type derived from the diamond-structure and crystallizes in space group $I4_1cd$ with lattice parameters $a = 13.6965(5)$ Å and $c = 7.7729(5)$ Å, $Z = 16$ (rotation method data acquisition using ω and φ scans, $R_1 = 0.0191$, w$R_2 = 0.0403$). Cu and Re atoms are tetrahedrally coordinated by O atoms, these tetrahedra are corner-shared, forming spirally twisted rings of 4-6-8-10-MeO_4 like Si_xO_y-rings in some silicon dioxide modifications or aluminosilicates. According to low-temperature powder X-ray diffraction and differential thermal analysis, $CuReO_4$ shows no phase transition down to 80 K and up to its melting point, 703 K.

Keywords: Copper(I) perrhenate; $CuReO_4$; Tetrahedra network; Acentric structure

1. Introduction

Up to now ternary oxides of all 3*d* elements with Re are known [1–9]. The oxides with Re^{7+}, the perrhenates, are easily prepared and therefore the most frequently investigated compounds. They are usually synthesized from aqueous solutions and are stable in air as hydrates. The crystal structures of all 3*d* metal perrhenates except Ti and Cr have been determined [1–4]. Ternary oxides with low valence Re ($< +7$) are usually prepared under extreme conditions (high-pressure high-temperature synthesis) [6–9]; the detailed crystal structure and magnetic properties are determined only for $CoReO_4$ [7], $MnReO_4$ [8], and $V_{0.5}Re_{0.5}O_2$ [9]. $MnReO_4$ has a monoclinic wolframite-type structure with octahedral coordination of Mn^{2+} and Re^{6+}. The same structure type was proposed by Sleight [6] for $ZnReO_4$. A compound $CuReO_4$ with Cu^{2+} is not known, but could also be expected in a wolframite-like structure due to similar Cu^{2+} and Zn^{2+} ionic radii for coordination number 6 (0.73 and 0.74 Å, respectively [10]).

In the Cu–Re–O–system the copper(II) perrhenate, $Cu(ReO_4)_2$, has been reported in the literature [5], and the crystal structure has been solved only for the crystallohydrate $Cu(ReO_4)_2 \cdot 4H_2O$ [2]. A few studies were devoted to copper(I) perrhenate, $CuReO_4$ [11–13]. It was prepared for the first time as a non-single-phase sample by thermal decomposition of $Cu(ReO_4)_2$ in vacuum [11] at 400–500 °C, its density and melting point have been determined, but neither crystal structure nor cell parameters were examined. Other authors [12] reported the synthesis of $CuReO_4$ from Cu and $Cu(ReO_4)_2$ at 360 °C, but no physical–chemical properties have been studied due to the presence of impurities in the sample. In this work [13] the authors used mass-spectrometric methods to measure the composition of the gaseous phase and vapor pressure over the sample containing about 80% $CuReO_4$, prepared from $Cu(ReO_4)_2$ and Cu. It was found that the vapor over $CuReO_4$ at 650–780 K consists of Re_2O_7 and $(CuReO_4)_2$ molecules. The impurity in the $CuReO_4$ sample was not identified. Neither crystal structure nor cell parameter were determined. From the literature it is unclear whether the authors of [11–13] have investigated the same compound $CuReO_4$, because two phases with nominal composition $CuReO_4$ and different oxidation states of metals ($+1$ and $+7$ or $+2$ and $+6$) could exist and no diffraction data have been presented. In this work we describe the synthesis of single-phase $CuReO_4$

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($Cu^{1+}Re^{7+}O_4$), its crystal structure and some physical–chemical properties.

2. Experimental

2.1. Syntheses

Since no synthesis methods of single-phase $CuReO_4$ are reported in the literature, different approaches have been tried. Samples of nominal composition $CuReO_4$ were synthesized in a sealed silica tube using Cu and Re oxides in different oxidation states: CuO (Chempur, 99.99%) and ReO_3 (Strem Chemicals, 99.9%) (I), Cu (Alfa Aesar, 99.99%) and freshly prepared $Cu(ReO_4)_2$ (II), Cu_2O (Alfa Aesar, 99.9%) and Re_2O_7 (Alfa Aesar, 99.9%) (III). Before use, CuO and ReO_3 were dried in air at 110–120 °C for 2–3 h. The synthesis conditions listed below were tested to achieve the best quality of the samples:

(I) A stoichiometric mixture of CuO and ReO_3 was ground in an agate mortar under acetone and pressed into pellets, which were placed in a quartz crucible and sealed in an evacuated silica tube.
(II) Stoichiometric amounts of $Cu(ReO_4)_2$ and Cu were weighed in a glove box (<1 ppm O_2/H_2O), mixed and pressed into pellets. $Cu(ReO_4)_2$ was prepared from copper(II) basic carbonate (Aldrich) and $HReO_4$ by a standard method described elsewhere [1]. $HReO_4$ was obtained from Re powder (Stream, 99.99%) and 30% solution of H_2O_2 (Aldrich, p.a.). In order to dehydrate pellets of $Cu(ReO_4)_2 \cdot 4H_2O$, they were held in dynamic vacuum at 140–160 °C during 2–3 h until the increase of temperature by 10° did not influence the residual pressure. Pellets of the mixture of $Cu(ReO_4)_2$ and Cu in a quartz crucible were placed into a silica tube, which was evacuated and sealed.
(III) A powder mixture of Cu_2O and Re_2O_7 oxides in the molar ratio 1:1 was placed within a glove box into a silica tube using a quartz crucible. The tube was sealed under vacuum.

In all cases the reactants were heated at 500–800 °C for 20–30 h.

2.2. Single-crystal X-ray diffraction

The crystal structure of $CuReO_4$ was solved by single-crystal X-ray diffraction using the Xcalibur system from Oxford Diffraction. The software packages SHELXS [14] and SHELXL [15] were used for structure solution and refinement as included in X-STEP32 [16]. A combined empirical absorption correction with frame scaling was applied, using the SCALE3 ABSPACK command in CrysalisRed [17].

2.3. X-ray powder diffraction (XPD) at room temperature and 80 K

Phase analysis and determination of cell parameters were carried out using XPD with a STOE STADI P diffractometer (Mo$K\alpha_1$-radiation, $\lambda = 0.7093$ Å) in steps of 0.02° for 2θ from 3° to 45° in transmission mode for flat samples or in Debye–Scherrer mode for sealed glass capillaries. All diffraction patterns have been analyzed by full-profile Rietveld refinements, using the software package WinPLOTR [18]. An Oxford Cryosystems Cryostream Cooler (600 Series) with nitrogen gas low temperature attachment was used for the cooling of a ground powder sample in sealed glass capillary of 0.3 mm diameter down to 80 K and stabilized for the collection of X-ray data.

2.4. EDX analysis

The cation composition was verified by EDX analysis, performed on different crystallites, using a Philips XL30 FEG microscope.

2.5. Differential thermal analysis (DTA-TG)

A simultaneous thermal analyzer NETZSCH STA 429 (CD) operated with dry and purified Ar was used to register mass loss and thermal flux curves. About 70 mg of $CuReO_4$ were heated in a Pt–Ir-crucible with a rate of 10 °C/min from 20 up to 1070 °C.

2.6. Infrared spectroscopy (IRS)

The infrared absorbtion spectrum of $CuReO_4$ was obtained on a PERKIN ELMER FTIR 1750-spectrometer. Samples were pressed into pellets, diluted with KBr. Pellets of pure KBr were used as negative control.

2.7. Magnetic susceptibility

The magnetic properties of $CuReO_4$ have been studied with a superconducting quantum interference device (SQUID) from quantum design. Measurements were performed in the temperature range from 1.8 to 250 K and field strength 50 and 500 Oe.

3. Results and discussion

3.1. Synthesis and characterization of $CuReO_4$ samples

The $CuReO_4$ samples were synthesized in the interval of temperature 500–800 °C by three methods according to reactions:

$$CuO + ReO_3 = CuReO_4, \quad (1)$$

$$Cu + Cu(ReO_4)_2 = 2CuReO_4, \quad (2)$$

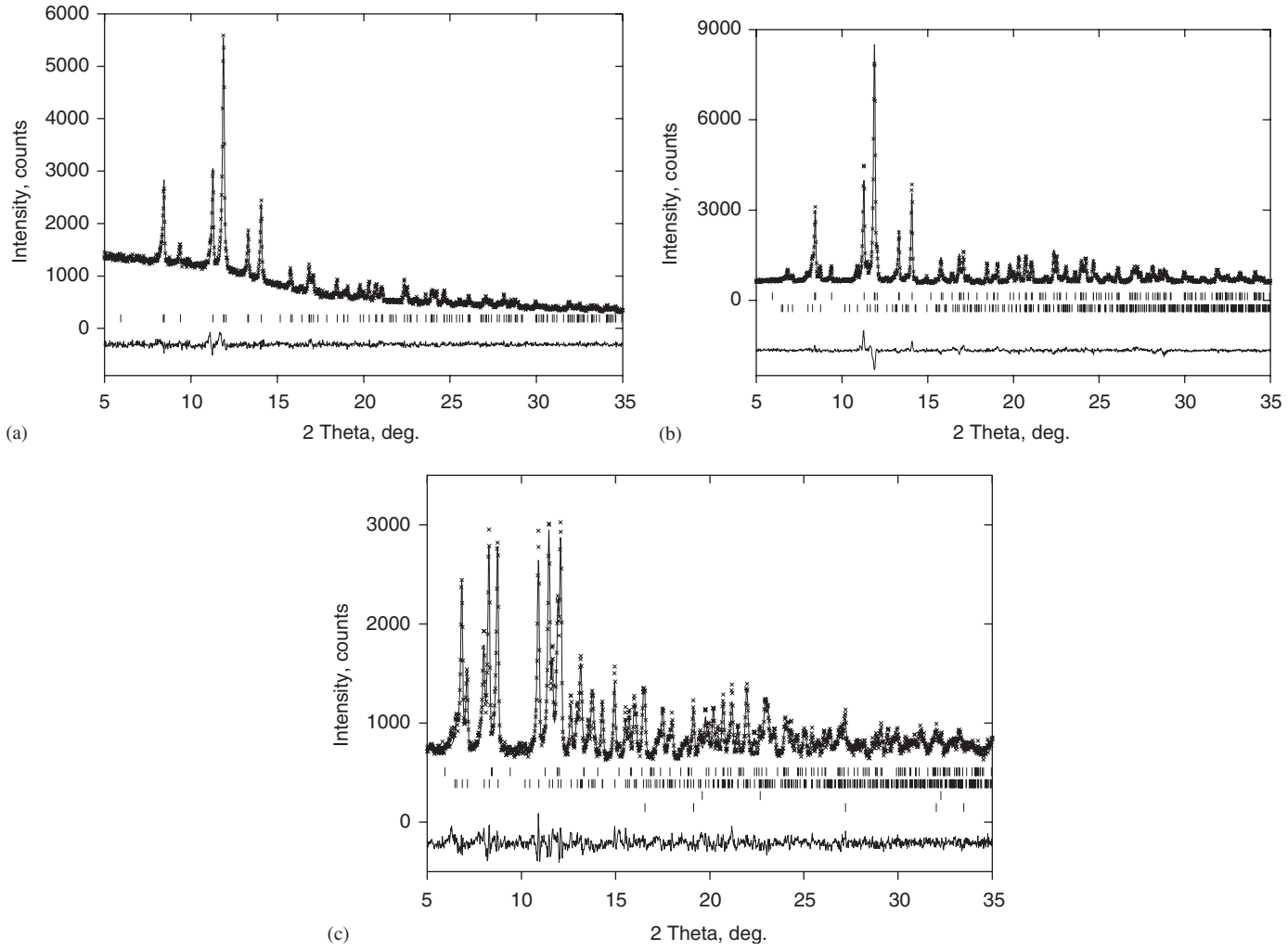

Fig. 1. The observed and fitted profiles for $CuReO_4$, together with the corresponding difference curve (Mo-$K\alpha_1$). (a) The sample was measured in a capillary, (b) the sample was measured during 3 hours in air, (c) the sample was left one month in air before measuring, the fitted profiles belong to the phases $CuReO_4$, $Cu(ReO_4)_2 \cdot 4H_2O$, Cu and Cu_2O (from top to bottom, respectively).

$$Cu_2O + Re_2O_7 = 2CuReO_4. \quad (3)$$

They appeared as dark-brown cakes, which indicated the occurrence of melting during syntheses. The breaking of these cakes yielded orange-red crystals. All samples gave similar XPD patterns, and all reflections were explained based on a tetragonal unit cell with lattice parameters $a = 13.69$ Å and $c = 7.77$ Å. Fig. 1(a) shows the diffraction pattern of the sample prepared by reaction (3).

The Re_2O_7 partial pressure over $CuReO_4$ calculated from the equation $\lg p(Re_2O_7, Pa) = -9561/T + 11.82$ [13], is 8×10^{-3} atm at 800 °C, corresponding to $\sim 6 \times 10^{-7}$ mol Re_2O_7 or 0.1 wt% Re of the overall Re mass in the reaction tube. At 500 °C it is ~0.00005 wt% Re. The EDX analysis of some thin $CuReO_4$ fragments of the sample, prepared at 800 °C, indicated that the average metal ratio Cu:Re is 1:1, in agreement with nominal composition (data not shown). The compound appears to be diamagnetic, because no distinct magnetic signal from $CuReO_4$ was registered at SQUID at field strengths 50 and 500 Oe.

The reaction with water was used to proof the oxidation states of Cu and Re, since the precipitate of a compound, containing Cu^{2+} and Re^{6+} would consist of ReO_2, because all compounds with Re^{6+} disproportionate in aqueous solution in ReO_4^- and ReO_2. On the other hand, Cu is expected to precipitate in the solution of a Cu^{1+} containing compound [19]. $CuReO_4$ decomposes in water immediately forming a precipitate of Cu_2O and Cu, according to the X-ray diffraction, and $Cu(ReO_4)_2$ in solution. Therefore, the oxidation states Cu^{1+}/Re^{7+} were assigned in agreement with no detectable paramagnetic moment.

Note that $CuReO_4$ is unstable to oxygen and moisture, and 15–20 wt% of $Cu(ReO_4)_2$ as impurity were present in XPD patterns of samples, which have been measured in air during 2–3 h (Fig. 1(b)). A sample of $CuReO_4$ kept one month in air (Fig. 1(c)) contained more than 90% $Cu(ReO_4)_2 \cdot 4H_2O$, only 2% $CuReO_4$, 4% Cu_2O and less than 1% Cu. No degradation was observed for a sample, measured in a glass capillary sealed under argon atmosphere (i.e. 100% $CuReO_4$) (Fig. 1(a)). The behavior of

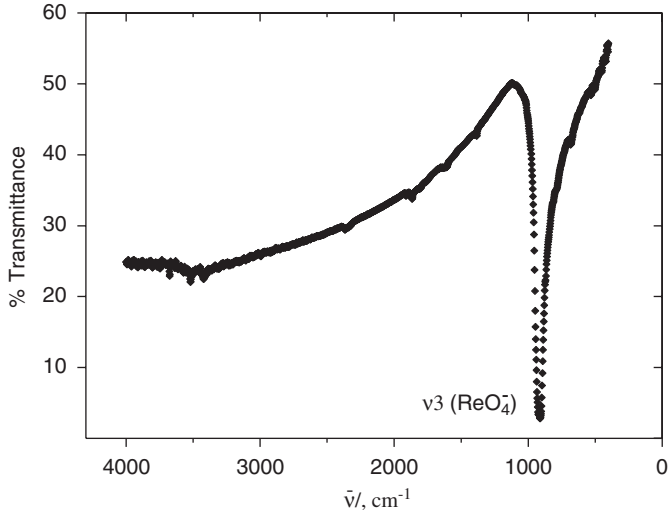

Fig. 2. The infrared spectrum of $CuReO_4$.

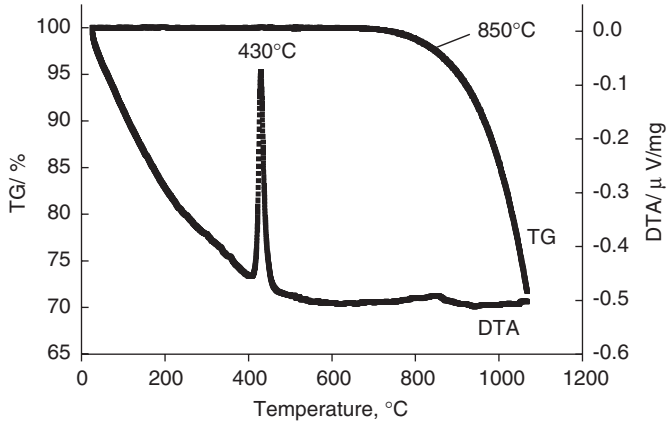

Fig. 3. TGA data of $CuReO_4$.

Table 1
Details of X-ray single-crystal data collection and structure refinement of $CuReO_4$

Crystal data	
Chemical formula	CuO_4Re
Formula weight	313.74
Crystal system	Tetragonal
Space group	$I4_1cd$
Unit-cell dimensions	$a = 13.6965(5)$ Å, $c = 7.7729(5)$ Å
Cell volume	1458.15(12) Å^3
Z	16
Calculated density (g/cm^3)	5.716
Temperature	293(2) K
Crystal form, color	Prism, red
Crystal size (mm)	$0.05 \times 0.05 \times 0.18$
Data collection	
Diffractometer	Oxford diffraction Xcalibur (TM); single-crystal X-ray diffractometer with sapphire CCD detector
Data collection method	Rotation method data acquisition using ω and φ scans(s)
Radiation type	Mo$K\alpha$ ($\lambda = 0.71073$ Å)
No. of reflections for cell parameters	1309
Absorption coefficient	38.855 mm^{-1}
$F(000)$	2176
θ range for data collection	2.97 to 26.36°
Range of h, k, l	$-16 \leqslant h \leqslant 16$, $-17 \leqslant k \leqslant 16$, $-9 \leqslant l \leqslant 9$
Reflections collected/unique	2084/662 [$R_{int} = 0.0199$]
Completeness to $\theta = 26.36°$	99.3%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	662/1/55
Goodness-of-fit on F^2	1.104
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0180$, w$R_2 = 0.0400$
R indices (all data)	$R_1 = 0.0191$, w$R_2 = 0.0403$
Absolute structure parameter	−0.01(2)
Largest diff. peak and hole	1.165 and −0.814 e/Å^3

copper(I) perrhenate in air differs from copper(I) halides CuX (X = Cl, Br, I), which are more stable and oxidize according to the reaction $2CuX + H_2O + 1/2O_2 = 2Cu(OH)X$ [19].

The IR-spectrum of $CuReO_4$ in the interval of 4000–500 cm^{-1} contains only one peak at ~920 cm^{-1} (Fig. 2), which corresponds to the ν3-vibration of the tetrahedral ion ReO_4^- [20] (Figs. 2 and 6).

The TGA data of $CuReO_4$ are presented in Fig. 3. The DTA-curve shows two endothermic peaks, the one at 430 °C is due to the melting of $CuReO_4$ and the other above 850 °C corresponds to an evaporation of $CuReO_4$ and in part to the decomposition of the sample to Cu_2O and Re_2O_7(g). The residue after the measurement consisted only of $CuReO_4$. This indicates an evaporation of $CuReO_4$ according to the reaction $2CuReO_4(s) = (CuReO_4)_2(g)$, which is known for alkali-metal perrhenates [21]. This result does not confirm previous findings [13], who reported the presence of Re_2O_7 in significant amount in the gas phase over $CuReO_4$ according to the reaction $2CuReO_4(s) = Cu_2O(s) + Re_2O_7(g)$. Our value of the melting point is 56° higher than the value obtained in the work [11]. This may be due to impurities in the sample of [11]. In contrast to Cu(I) halides $CuReO_4$ has no phase transition before the melting point [22].

3.2. Crystal structure of $CuReO_4$

A tetragonal unit cell with $a = 13.6965(5)$ Å and $c = 7.7729(5)$ Å was determined by X-ray single-crystal structure analysis for the sample synthesized at 800 °C and slowly cooled in the furnace. The structure was solved and refined in space group $I4_1cd$ (see Table 1). Positional parameters and selected interatomic distances for $CuReO_4$ are listed in Tables 2 and 3, respectively.

Since no data regarding compounds with analogous parameters were found in the ICSD [23], a new crystal structure type, the $CuReO_4$-type is established. Its structure represents a three-dimensional framework formed by tetrahedra of CuO_4 and ReO_4 connected by corner-sharing (Fig. 4). There is a number of large channels with an

Table 2
Positional and thermal displacement parameters ($Å^2$) for $CuReO_4$

Atom	Site	x	y	z	Occup.
Re	16*b*	0.90191(2)	0.35603(2)	0.25138(11)	1
Cu	16*b*	0.1671(1)	0.3809(1)	0.3179(2)	1
O(1)	16*b*	0.8756(5)	0.2617(5)	0.3888(9)	1
O(2)	16*b*	0.0253(5)	0.3615(5)	0.2151(14)	1
O(3)	16*b*	0.8441(6)	0.3373(6)	0.0553(9)	1
O(4)	16*b*	0.8610(5)	0.4632(5)	0.3435(12)	1

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Re	0.0246(2)	0.0199(2)	0.0251(2)	−0.0004(1)	−0.0004(2)	0.0022(2)
Cu	0.0498(8)	0.0529(8)	0.0376(8)	−0.0037(7)	0.0182(7)	0.0034(7)
O(1)	0.057(5)	0.026(3)	0.030(4)	0.004(4)	0.003(4)	0.000(3)
O(2)	0.018(4)	0.069(5)	0.077(7)	−0.002(3)	0.000(4)	−0.009(5)
O(3)	0.048(4)	0.047(4)	0.025(5)	−0.003(4)	−0.005(3)	0.006(3)
O(4)	0.059(5)	0.023(4)	0.063(5)	0.000(3)	0.008(4)	−0.001(4)

Table 3
Characteristic geometric parameters (Å, deg) for $CuReO_4$

Re–O(1)	1.715(7)	O(1)-Re-O(2)	110.0(3)	O(3)-Cu-O(2)	104.3(4)
Re–O(2)	1.715(7)	O(1)–Re–O(4)	108.3(3)	O(1)–Cu–O(4)	100.9(2)
Re–O(3)	1.727(7)	O(2)–Re–O(4)	110.5(3)	O(3)–Cu–O(4)	101.5(3)
Re–O(4)	1.737(7)	O(1)–Re–O(3)	109.9(3)	O(2)–Cu–O(4)	89.7(3)
Cu–O(1)	1.903(7)	O(2)–Re–O(3)	108.2(4)	Re–O(1)–Cu	163.9(4)
Cu–O(2)	2.117(8)	O(4)–Re–O(3)	110.0(4)	Re–O(2)–Cu	147.9(4)
Cu–O(3)	1.945(7)	O(1)–Cu–O(3)	99.5(3)	Re–O(3)–Cu	145.4(4)
Cu–O(4)	2.179(7)	O(1)–Cu–O(2)	151.4(2)	Re–O(4)–Cu	148.5(4)

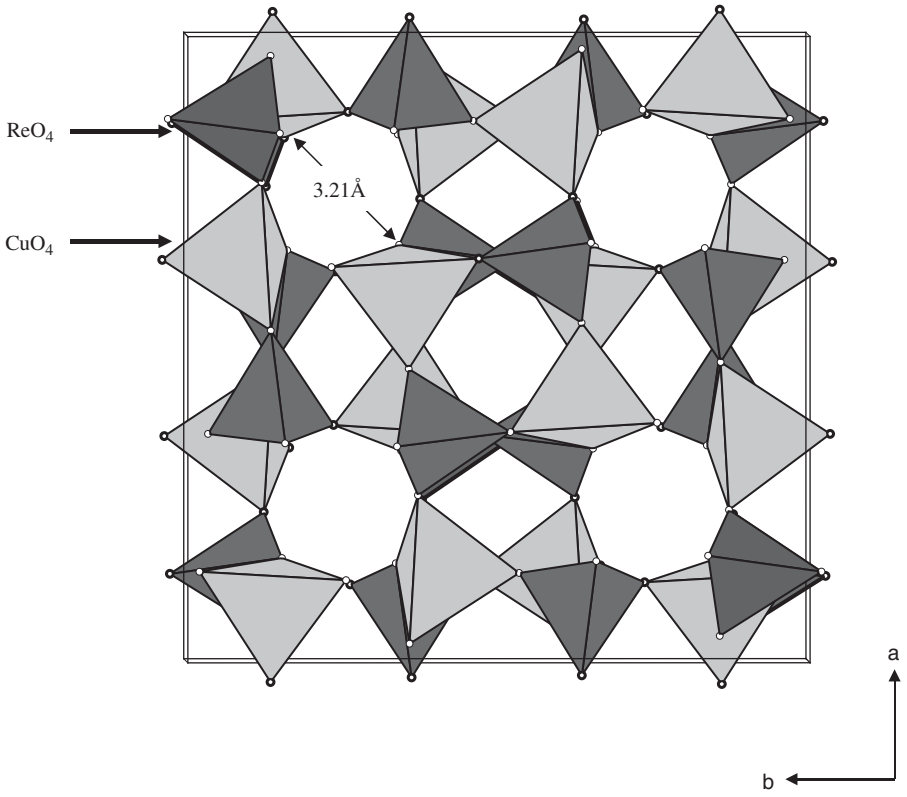

Fig. 4. The crystal structure of $CuReO_4$. Dark gray tetrahedra are occupied by Re atoms, light gray by Cu atoms.

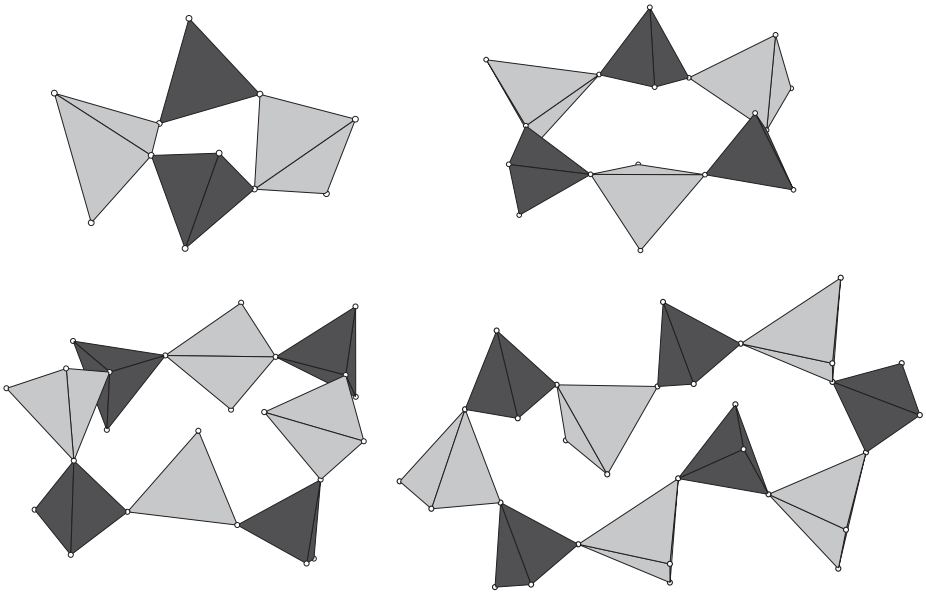

Fig. 5. 4-6-8-10-membered-rings in the framework of MO_4-tetrahedra in $CuReO_4$.

average diameter of 3.1 Å between these tetrahedra. It can be suggested that these large channels in the structure facilitate the degradation of $CuReO_4$ in air.

The structure of $CuReO_4$ can be considered as derived from the diamond-structure and is similar to structures of some silicon dioxides and aluminosilicates [19,24]: the CuO_4- and ReO_4-tetrahedra form spirally twisted rings of 4-6-8-10-MeO_4-tetrahedra (Fig. 5) like 6-silica–rings in β-crystobalite or 4-6-8-10-alumo-silica-rings in feldspar $R^+[AlSi_3O_8]$ or $R^{2+}[Al_2Si_2O_8]$ [24].

All atoms in the structure occupy the same site symmetry (16*b*); each ReO_4-tetrahedron is surrounded by 4 CuO_4-tetrahedra, and vice versa. This sequence of tetrahedra is subjected to the *Loewenstein-rule*, which has been found for aluminosilicates: ReO_4-tetrahedra are never bounded with each other, the structural fragment Re–O–Re is avoided [25]. Some interatomic distances and bond angles are listed in Table 3. ReO_4-tetrahedra are practically undistorted: $d_{Re-O} = 1.715–1.737$ Å, the angles O–Re–O = 108.15–110.54°. The average Re–O distance ($d_{Re-O} = 1.724$ Å) is in very good agreement with Re–O-distances for Re^{7+} located in a tetrahedron of oxygen atoms in Re_2O_7 (1.70–1.80 Å) [26], in alkali-metal perrhenates $MReO_4$ (M = K, $d_{Re-O} = 1.736$ Å [27], M = Rb, $d_{Re-O} = 1.722$ Å [28]), in vanadyl perrhenate $VO(ReO_4)_2$ (1.69–1.75 Å) [29] or in $Cu(ReO_4)_2$ (1.69–1.74 Å) [2] (Fig. 6).

The coordination environment of Cu is moderately distorted from ideal tetrahedral symmetry with O–Cu–O bond angles (Table 3) ranging from 90° to 151° and bond lengths $d_{Cu-O} = 1.903–2.179$ Å. The average distance ($d_{Cu-O} = 2.036$ Å) is significantly larger than $d_{Cu-O} = 1.85$ Å in cuprite Cu_2O (linear oxygen coordination of Cu atoms) and similar to the distance Cu–O (1.993 and 2.031 Å) in NaCuO (linear oxygen coordination of Cu atoms, too) [30].

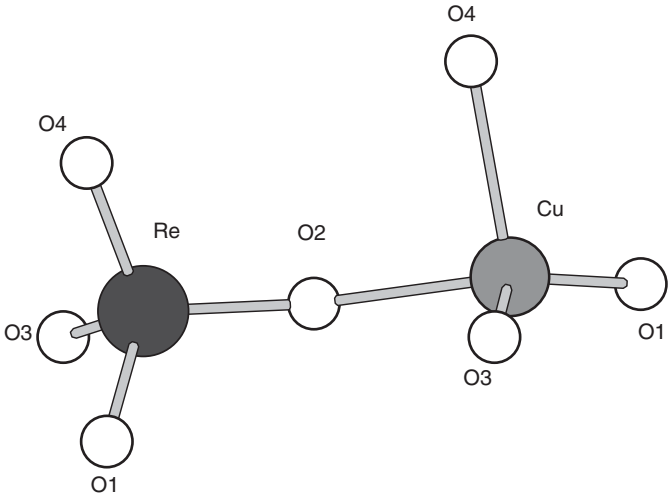

Fig. 6. Oxygen coordination around Cu and Re atoms

A tetrahedral coordination is not unusual for Re(VII) and Cu(I) cations (for instance, CuX, where X = Cl, Br, J [19,22]), but there are no examples of CuO_4 tetrahedra for simple copper(I) compounds [22]. It is interesting to see, how the relative size of cations M^+ in $MReO_4$ influences the structural chemistry of perrhenates of monovalent metals (Table 4). For example, perrhenates of alkali metals ($M = Na^+$, K^+, Rb^+) and the silver perrhenate $AgReO_4$ crystallize in a scheelite-type tetragonal structure, in which M atoms occupy dodecahedra of O atoms connected by edge-sharing [27,28,31,32]. The thallium(I) and cesium perrhenates, $TlReO_4$ [33] and $CsReO_4$ [34], crystallize at ambient pressure in a scheelite-like orthorhombic structure with dodecahedric coordination of Tl and Cs. $LiReO_4$ and $CuReO_4$ are the exception from this row due to their small radii, but they have different structures despite their similar

Table 4
Ionic radii and crystal structure types of some monovalent perrhenates, MReO$_4$

Ion	Ionic radius for coordination number 6 (Å) [10]	Structural type at room temperature	Coordination polyhedron	Space group	Average M–O bond length (Å)
Li^+	0.76	$LiReO_4$	Trigonal bipyramid and trigonal pyramid	*P*-1	2.090
					2.065
Cu^+	0.77	$CuReO_4$	Tetrahedron	$I4_1cd$	2.025
Na^+	1.02	Scheelite	Dodecahedron	$I4_1/a$	2.582
Ag^+	1.15	Scheelite	Dodecahedron	$I4_1/a$	2.591
K^+	1.38	Scheelite	Dodecahedron	$I4_1/a$	2.802
Tl^+	1.50	Scheelite-like	Dodecahedron	*Pnma*	2.936
Rb^+	1.52	Scheelite	Dodecahedron	$I4_1/a$	2.960
Cs^+	1.67	Scheelite-like	Dodecahedron	*Pnma*	3.184

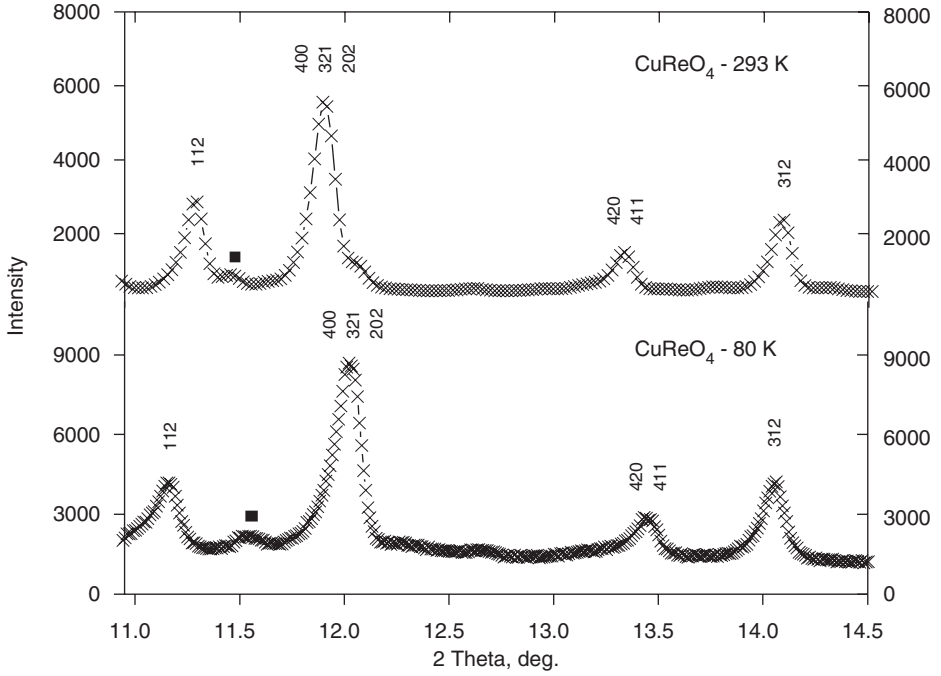

Fig. 7. Selected fragments of the X-ray pattern of $CuReO_4$ at different temperatures. The symbol * indicates the contributions from the impurity $Cu(ReO_4)_2$ formed due to sample handling in air.

sizes: Li^+ ions occupy in the structure three different crystallographic positions with a distorted trigonal bipyramid and distorted trigonal pyramid from oxygen atoms [35]. Re atoms are tetrahedrically surrounded by O in all these cases. The critical average bond length *M*–O to stabilize the scheelite-type structure seems to be more than 2.5 Å, which corresponds to an ionic radius of more than 1 Å. Note that all these structures exept $CuReO_4$ are centric structures.

3.3. X-ray diffraction of $CuReO_4$ at low temperature

A sample for X-ray diffraction at 80 K was prepared from CuO and ReO_3 at 600 °C with quenching after the synthesis. The diffraction pattern showed no additional peaks in comparison with the pattern at 293 K. In both cases there is a small quantity of $Cu(ReO_4)_2$ in the sample due to sample preparation for analysis in air. Fig. 7 shows two fragments of two diffraction patterns of the same sample $CuReO_4$ measured at 293 and 80 K. A distinct peak shift can be seen with decrease of temperature, which indicates a temperature-dependent change of unit cell parameters.

Applying the structure of $CuReO_4$ at room temperature as a starting model, a Rietveld refinement of all atomic positions at 80 K was performed with an isotropic approximation for the thermal displacement parameters. The *z*-coordinate of Re as the heaviest atom in the structure

was fixed at 0.00. Thermal displacement parameters for all oxygen atoms were fixed at 1.0 $Å^2$ and thermal parameters for the cations were refined separately. After the final refinement good values for the reliability factors were obtained: $R_p = 2.81\%$, $R_{wp} = 3.60\%$, $\chi^2 = 1.70$. The parameters "*a*" and "*b*" and the cell volume decrease with decreasing temperature whereas the "*c*" parameter increases: $a = 13.6812(4)$ Å, $c = 7.7615(3)$ Å, $V = 1452.76(7)$ $Å^3$ (293K) and $a = 13.5118(3)$ Å, $c = 7.8782(2)$ Å, $V = 1438.31(5)$ $Å^3$ (80 K). The average Re–O-distance increases from 1.743 to 1.843 Å, whereas the average Cu–O-distance decreases from 2.025 to 1.969 Å.

Further details of the crystal structure investigation can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, (fax: +49 7247 808 666; *e-mail*: crysdata@fiz.karlsruhe.de) on quoting the depository number CSD 416510.

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References

[1] A. Butz, G. Miehe, H. Paulus, P. Strauss, H. Fuess, J. Solid State Chem. 138 (1998) 232.
[2] M. Varfolomeev, A. Zemenkova, V. Chrustalev, Ju. Struckov, H.-J. Lunk, B. Ziemer, J. Alloy Compd. 215 (1994) 339.
[3] C. Mujica, K. Peters, E.-M. Peters, H.G. von Schnering, Z. Kristallogr.—New Cryst. St. 213 (1998) 11.
[4] C. Mujica, K. Peters, E.-M. Peters, W. Carillo, H.G. von Schnering, Bol. Soc. Chil. Quim. 44 (1999) 161.
[5] L. Zeitseva, et al., Russ. J. Inorg. Chem. 22 (1977) 1185 (Engl. Transl.).
[6] A.W. Sleight, Inorg. Chem. 14 (1975) 597.
[7] W.H. Baur, W. Joswig, G. Pieper, D. Kassner, J. Solid State Chem. 99 (1992) 207.
[8] K.G. Bramnik, H. Ehrenberg, S. Buhre, H. Fuess, Acta Crystallogr. B 61 (2005) 246.
[9] K.G. Bramnik, H. Ehrenberg, R. Theissmann, H. Fuess, E. Moran, Z. Kristallogr. 218 (2003) 455.
[10] R.D. Shannon, Acta Crystallogr. A 32 (1976) 751.
[11] W.T. Smith, J. Am. Chem. Soc. 73 (1951) 77.
[12] J. Cloarec, A. Deschanvres, B. Raveau, C. R. Acad. Sci. II 264 (1967) 1841.
[13] K. Skudlarski, W. Lukas, Rocz. Chem. 48 (1974) 745.
[14] G.M. Sheldrick, Acta Crystallogr. A 46 (1990) 467.
[15] G.M. Sheldrick, SHELXL97, Program for the Refinement of Crystal Structures, University of Göttingen, Germany, 1997.
[16] Stoe & Cie, X-STEP32, Stoe & Cie GmbH, Darmstadt, Germany, 2000.
[17] CrysalisRed, CCD data reduction GUI, Version 1.171.26, Oxford Diffraction Poland, 2005.
[18] T. Roisnel, J. Rodriguez-Carvajal, Mater. Sci. Forum 378–381 (2001) 118.
[19] A.F. Holleman, E. Wiberg, Lehrbuch der Anorganischen Chemie, Walter de Gruyter, Berlin, 1985, p. 1451s.
[20] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, Parts I, II, Wiley, New York, 1997.
[21] Ye.K. Kazenas, Vaporization Thermodynamics of Double Oxides, Nauka, Moscow, 2004, p. 551s (in Russian).
[22] A.W. Wells, Structural Inorganic Chemistry, fifth ed., Clarendon Press, Oxford, 1984.
[23] Inorganic Crystal Structure Database (ICSD), Fachinformationszentrum Karlsruhe, Germany, 2005.
[24] A. Petzold, W. Hinz, Silikatchemie, Ferdinand Enke Verlag, Stuttgart, 1979, p. 219s.
[25] W. Loewenstein, Am. Miner. 39 (1954) 92.
[26] B. Krebs, A. Mueller, H.H. Beyer, Inorg. Chem. 8 (1969) 436.
[27] J.C. Brown, B.M. Powell, S.N. Stuart, Acta Crystallogr. C 49 (1993) 214.
[28] P. Roegner, K.-J. Range, Z. Naturforsch. B 48 (1993) 233.
[29] B. Bastide, R. Enjalbert, H. Fuess, J. Galy, Solid State Sci. 2 (2000) 545.
[30] R. Hoppe, K. Hestermann, F. Schenk, Z. Anorg. Allg. Chem. 367 (1969) 275.
[31] A. Atzesdorfer, K.-J. Range, Z. Naturforsch. B 50 (1995) 1417.
[32] D. Yu. Naumov, A.V. Virovets, S.V. Korenev, A.I. Gubanov, Acta Crystallogr. C 55 (1999) 8.
[33] A. Jayaraman, G.A. Kourouklis, R.M. Fleming, L.G. Van Uitert, Phys. Rev. B 37 (1) (1988) 664.
[34] P. Roegner, K.-J. Range, Z. Naturforsch. B 48 (1993) 685.
[35] T. Betz, R. Hoppe, Z. Anorg. Allg. Chem. 500 (1983) 23.