Short Communication

Synthesis and Structure of the Perovskite-Type Phase $Ba_4CuYW_2O_{12}$

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Since the discovery of high-T_c superconducting phases in the BaO–CuO–Y_2O_3 system,[1] substitutions in this system have been of interest. A substitution of tungsten for copper has recently been discussed.[2]

We present here a cubic perovskite-type phase of the formula $Ba_4CuYW_2O_{12}$, with a cell parameter close to that reported for a supposedly superconducting phase, and a volume eight times the primitive perovskite unit.

Phase analysis. The starting chemicals, $BaCO_3$ (Merck, p.a.), CuO (Schering, p.a.), Y_2O_3 (Starck, finest) and WO_3 (Riedel de Haën, puriss), were ground together and pelletized. The pellets were placed in an alumina crucible, heated to 1000 °C for about 24 h and cooled outside the furnace. The products were brown powders, and no reaction with the crucible could be noticed.

The X-ray powder patterns were taken in a Guinier–Hägg focussing camera with Si as internal standard (a_{Si} = 5.430 88 Å at 25 °C), and the films were automatically scanned.[3] Starting compositions corresponding to $Ba_2Cu_2YWO_{8.5}$ gave clearly polyphasic samples.

However, when the composition was close to the ratio Ba:Cu:Y:W = 4:1:1:2 the Guinier film showed a cubic pattern with only one very weak extra line. The pattern was indexed on the basis of a face-centred cell with a = 8.306 5 (6) Å (Table 1).

Part of this sample was ground in butanol and placed on a holey carbon film on top of a pure nickel grid. The crystal fragments were analyzed in a JEOL 2000FX transmission electron microscope equipped with a standard EDS detector at the 70° take-off position (LINK QX200). Selected-area electron diffraction along the <100> zone axis was compatible with a cubic F-centred cell with $a \approx 8.3$ Å. Reflections $hk0$ with $h + k = 4n$ were markedly stronger than the rest. The EDS analyses of a large number of thin fragments indicated that the weighted-in stoichiometry was preserved, and no impurities could be detected. All crystals analyzed gave roughly the same metal ratio.

A sample of the unreacted powder (26.73 mg) was heated in air in a Perkin Elmer thermogravimetry apparatus. The heating rate was 2 °C min^{-1} in the temperature range 500–1000 °C. The measured loss of weight in this experiment was 12.9 %. If the total reaction is assumed to be given by reaction (1), the loss of weight should be 12.7 %. The small difference between this calculated value and the one measured could be explained by moisture or a slight volatilazation of WO_3.

$$8BaCO_3 + 2CuO + Y_2O_3 + 4WO_3 \rightarrow 2Ba_4CuYW_2O_{12} + 8CO_2 + \tfrac{1}{2}O_2 \quad (1)$$

Structure refinement. Since the composition was found to be close to that of an ideal perovskite, ABO_3, we assumed barium to be in the A-position and the smaller atoms cop-

Table 1. Observed and calculated d-values for the Guinier–Hägg X-ray powder diffraction pattern of $Ba_4CuYW_2O_{12}$. The observed and calculated intensities are from a Rietveld refinement based on data obtained from a STOE powder diffractometer. λ = 1.540 598 Å.

h	k	l	d_{obs}/Å	d_{calc}/Å	I_{obs}	I_{calc}
1	1	1	4.7976	4.7957	12.5	12.0
2	0	0	4.1518	4.1532	0.9	0.7
2	2	0	2.9360	2.9368	100.0	100.0
3	1	1	2.5038	2.5045	6.1	5.5
2	2	2	2.3973	2.3979	2.5	2.2
4	0	0	2.0768	2.0766	27.0	28.1
3	3	1	1.9054	1.9056	1.8	2.0
4	2	2	1.6958	1.6955	37.7	37.4
3	3	3	1.5993	1.5986	2.6	2.6
5	1	1				
4	4	0	1.4688	1.4684	15.6	16.0
5	3	1	1.4045	1.4040	1.6	2.5
6	2	0	1.3137	1.3134	14.7	15.6
5	3	3	1.2669	1.2667	0.9	0.8
4	4	4	1.1989	1.1989	5.4	4.9
5	5	1	1.1626	1.1631	1.9	1.4
7	1	1				
6	4	2	1.1099	1.1100	17.7	17.7

Table 2. Positional parameters of $Ba_4CuYW_2O_{12}$ and individual isotropic temperature factors, with estimated standard deviations in parentheses.

Atom	Position	*x/a*	*y/b*	*z/c*	*B*/Å^2
W	4(*a*)	0	0	0	1.0(2)
Cu,Y	4(*b*)	1/2	1/2	1/2	2.8(3)
Ba	8(*c*)	1/4	1/4	1/4	0.4(1)
O	24(*e*)	0.232(3)	0	0	1.7(4)

per, yttrium and tungsten in the *B*-positions. *Fm*3*m* is then a possible space group if Cu and Y are statistically distributed in 4*b* and four W located in 4*a* (Table 2).

X-ray powder data for Rietveld refinement were collected on a STOE STADI/P powder diffractometer, using a rotating sample in a symmetric transmission mode. Step intensities in the 2θ-range 10–120° were used in the refinement (step length $\Delta 2\theta = 0.02°$).

Full-profile Rietveld refinement of the structure was carried out with the program DBW3.2S.[4] The following parameters were refined: one positional parameter, five isotropic temperature factors, one zero-point parameter, one scale factor and three half-width parameters. It was noticed that the maximum value for the half-widths was rather large, 0.65° (2θ). The refinement was terminated when all shifts in the parameters were less than 10 % of the corresponding standard deviations. The final *R*-values, $R_p = 0.046$, $R_{wp} = 0.060$, $R_{Bragg} = 0.048$ and $R_F = 0.068$, were obtained for the positional parameter and temperature factors in Table 2. Observed and calculated intensities are listed in Table 1. The bond lengths are Cu(Y)–6O = 2.23(3) Å, W–6O = 1.93(3) Å and Ba–12O = 2.941(1) Å.

In separate refinement cycles the occupation factors were checked. However, no significant deviation from the assumed formula was seen.

This new phase in the Ba–Cu–Y–W–O system is a member of the perovskite family Ba_2MWO_6 (*M* = Mg, Zn, Ni, Ca) reported by Filipev *et al.*[5] The refinement indicates that Cu and Y share the *M*-positions. It is probable that Cu(II) is reduced to Cu(I), as suggested by the brown colour of the phase and the thermogravimetry experiment. The relatively high temperature factors for Cu and Y indicate that the true positions of these atoms may deviate slightly from the average symmetrical sites. The sample was found to be a very poor electric conductor at room temperature.

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