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Crystal Structure of $DySr_2Cu_{2.7}Mo_{0.3}O_{7.2}$ and $DySr_2Cu_{2.7}Cr_{0.3}O_{7.2}$ Analogues of the 123 YBCO Phase

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The crystal structure of $DySr_2Cu_{2.7}Mo_{0.3}O_{7.2}$ and $DySr_2Cu_{2.7}Cr_{0.3}O_{7.2}$ was solved by the X-ray powder diffraction method. The space group of $DySr_2Cu_{2.7}Mo_{0.3}O_{7.2}$ ($M_r = 653.29$) is *P4/mmm*, with lattice parameters $a = 3.8262(1)$ Å, $c = 11.5492(2)$ Å, and $Z = 1$. The space group of $DySr_2Cu_{2.7}Cr_{0.3}O_{7.2}$ ($M_r = 640.11$) is *P4/mmm*, with lattice parameters $a = 3.8531(1)$ Å, $c = 11.3804(2)$ Å, and $Z = 1$. Rietveld refinement results in the discrepancy factors $R_B = 7.93$ and $R_{wp} = 3.76$ for the Mo compound and $R_B = 9.76$ and $R_{wp} = 4.07$ for the Cr compound. © 1998 Academic Press

Key Words: **oxides; 123-type phases; crystal structure; powder X-ray diffraction; Rietveld method.**

INTRODUCTION

At the end of the 1980s during the rash of research to discover new classes of high-temperature superconductors, the strontium analogues of the 123 YBCO phases were synthesized. In 1987 partial substitution of Ba by Sr in the 123 phase was carried out (1, 2). In 1990 Okai (3) managed to prepare pure, fully substituted $YSr_2Cu_3O_7$ at a high oxygen partial pressure (in excess of 6 GPa), but it has been known since 1989 that it is possible to obtain such phases at ambient pressure by partial replacement of Cu with Al, Fe, Co, and Pb (4). Later it was shown that several other cations may be used as well. For instance, in the system $YSr_2Cu_{3-x}Ga_xO_y$, a single phase may be obtained for $x = 0.4$–1.0 (5). However, it is known that even smaller amounts of some cations are sufficient to obtain a single phase (6–9). Replacing yttrium with lanthanoids may cause some differences in structure and equilibrium between single-phase and multiphase regions on the phase diagram. Since the single phase of $HoSr_2Cu_{2.7}Mo_{0.3}O_{7.54}$ had been obtained and its structure was solved (8), we decided to study its Dy analogues. To find out the influence of the replacement of molybdenum by chromium, we decided to investigate $DySr_2Cu_{2.7}Cr_{0.3}O_x$ as well.

The majority of compounds described in the literature have been synthesized at a temperature about 1050°C (5, 6, 9), but the Ho–Mo phase was obtained at 900°C. We chose the temperature 950°C to have better comparison with the Ho phase and to find out its influence on the synthesis of the Cr compound.

EXPERIMENTAL

Specimens were prepared by mixing appropriate molar proportions of dried Dy_2O_3, $SrCO_3$, CuO, and MoO_3 or $(NH_4)Cr_2O_7$ (analytical grade). To make the mixture homogenous, a small amount of acetone was added, and grinding was carried on in an agate mortar until the dispersant evaporated. The samples were heated in alumina crucibles in air at 950°C for 40 h. After cooling, which took about 2 h, the samples were removed and reground. Before the final X-ray picture was taken, heating and regrinding were repeated twice under the same conditions. X-ray diffraction patterns were obtained with Cu$K\alpha$ radiation (Ni filter) on a Philips PW3020 powder diffractometer (Bragg–Brentano geometry). To avoid texture, a back-loading technique was applied. Details of data collection and some crystallographic data are presented in Table 1. Volumetric analysis (10) of the samples was performed to establish the oxygen content. The numbers of oxygen atoms in the unit cell were found to be 7.23(2) and 7.25(2) for the Mo and Cr compounds, respectively (these values are averages from two measurements), on the condition that the samples consist of pure 123 phases. This assumption is not true for the Cr compound (see Structure Determination). Also the Mo sample may contain a small quantity of impurities not detectable by X-ray diffraction. Finally, taking into account the estimated accuracy of the method, the amount of oxygen in the formula was rounded to the first digit after the decimal point and the value of 7.2 was accepted for both specimens.

Dynamic magnetic susceptibility measurements showed that both samples fail to show superconductivity in the whole measured temperature range down to 11 K.

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TABLE 1
Crystallographic Parameters for $DySr_2Cu_{2.7}Mo_{0.3}O_{7.2}$ and $DySr_2Cu_{2.7}Cr_{0.3}O_{7.2}$

	$DySr_2Cu_{2.7}Mo_{0.3}O_{7.2}$	$DySr_2Cu_{2.7}Cr_{0.3}O_{7.2}$
Formula weight	653.29	640.11
Habit	Black powder	Black powder
Crystal system	Tetragonal	Tetragonal
a (Å)	3.8262(1)	3.8531(1)
c (Å)	11.5492(2)	11.3804(2)
V (Å^3)	169.078(3)	168.958(3)
Space group	$P4/mmm$	$P4/mmm$
Z	1	1
ρ_{calc} (g/cm^3)	6.49	6.32
Radiation	Cu$K\alpha$	Cu$K\alpha$
Applied filter	Ni	Ni
Start/stop angle (°2θ)	5.0/112.1	5.0/115.0
Step size (°2θ)	0.02	0.02
Number of excluded regions	Zero	Zero
R_F/R_B	10.03/7.93	14.18/9.76
R_p/R_{wp}	2.62/3.76	2.59/4.07
S	2.21	2.49

TABLE 2
Values of R Factors for Different Models

	$DySr_2Cu_{2.7}Mo_{0.3}O_{7.2}$			$DySr_2Cu_{2.7}Cr_{0.3}O_{7.2}$		
	$Pmmm$	$P4/mmm$	$P4/mmm$ + O1 shift	$Pmmm$	$P4/mmm$	$P4/mmm$ + O1 shift
R_B	9.41	9.77	7.93	11.60	12.23	9.76
R_F	10.04	10.41	10.03	13.90	14.42	14.18
R_{wp}	3.91	4.02	3.76	4.04	4.19	4.07

Structure Determination

The pure Mo 123-type phase was obtained after 80 h of heating. However, even after 120 h of heating at 950°C, there were three phases in the sample with chromium. The main phases were $DySr_2Cu_{2.7}Cr_{0.3}O_{7.2}$ and Dy_2O_3. In addition to the diffraction lines from these two phases, there were three lines in the diffraction pattern at $d = 2.811$, 2.987, and 2.118 Å with intensities (I) 4.2, 2.2, and 1.7%, respectively. They correspond to the strongest lines of $Sr_{14-y}Dy_yCu_{24}O_x$, but being weak, they were not taken into account during Rietveld calculations.

The weight fraction of Dy_2O_3 estimated by the Rietveld method was 5%. All refinements were carried out with the program DBWS (11).

Lattice parameters of both compounds were determined by the program package Proszki (12). The a and b values were very similar, suggesting tetragonal symmetry. To avoid a mistake, the structures were independently refined in $P4/mmm$ and $Pmmm$. The orthorhombic and tetragonal structures of $YBa_2Cu_3O_x$ were taken as models. The discrepancy factors for the refinements in both space groups are given in Table 2. The differences of appropriate R factors are small, in spite of the fact that in $Pmmm$ five more parameters are refined. Additionally, for both compounds tetragonal models with a shift of O1 from $0\,1/2\,0$ (mmm symmetry) to the $x\,1/2\,0$ ($m2m$ symmetry) were refined, thus adding one parameter. That resulted in significant R factor reduction (Table 2) and therefore both structures were finally refined in the tetragonal system with O1 having $m2m$ symmetry. The same model was used by Harrison for $HoSr_2Cu_{2.7}Mo_{0.3}O_{7.54}$ (8).

Copper in either of its positions may be replaced by molybdenum or chromium. Refinements carried out without conditions on Mo content and with a fixed amount of molybdenum resulted in a negative occupancy factor of Mo for the position $00z$. Since its value was nearly equal to zero, the occupancy factor for this position was assigned to zero as well. The refinement of the occupancy factor of Mo in the position 000 resulted in the value 0.45(2), which is more than it should be according to the stoichiometry of the sample.

Refinement with a fixed amount of chromium resulted in a negative occupancy factor of Cr in position 000. Therefore the occupancy factor for that chromium was assumed to be zero. The refinement of the occupancy factor for Cr in the position $00z$ resulted in a value two times larger than the stoichiometric one and it was fixed at a value of 0.15.

The occupancy of oxygen O(1) in the $x\,1/2\,0$ position in the Mo compound was refined to 0.36(2), which gave the quantity of oxygen in the specimen equal to 7.44. For the Cr compound the corresponding values were 0.35(2) and 7.41.

STRUCTURE DESCRIPTION

Plots of the observed and calculated patterns are presented in Figs. 1a and 1b. Atomic positions are given in Tables 3 and 4 and selected bond distances and bond angles are listed in Tables 5 and 6 respectively for the Mo and Cr compounds.

In Fig. 2a a schematic structure of $YBa_2Cu_3O_7$ is presented. The copper atom at site $1a$ (000) is coordinated by four oxygen atoms (in $YBa_2Cu_3O_6$ that atom is coordinated by two oxygens). In $DySr_2Cu_{2.7}Mo_{0.3}O_{7.2}$ and $DySr_2Cu_{2.7}Cr_{0.3}O_{7.2}$, the oxygen atoms are shifted from $2f$ to the $4n$ sites with a decrease of the occupancy factor, which means that each oxygen position is split into two new ones. This shift in $DySr_2Cu_{2.7}Mo_{0.3}O_{7.2}$ is much larger than that in the Cr phase (0.91(2) and 0.68(3) Å, respectively). In Fig. 2b the surroundings of the Cu(1) site in the Mo compound are shown as a strongly distorted octahedron, with eight vertices lying in the XY plane. Only less than half of them are occupied at a time. The Cu(1)–O(3) distance is rather

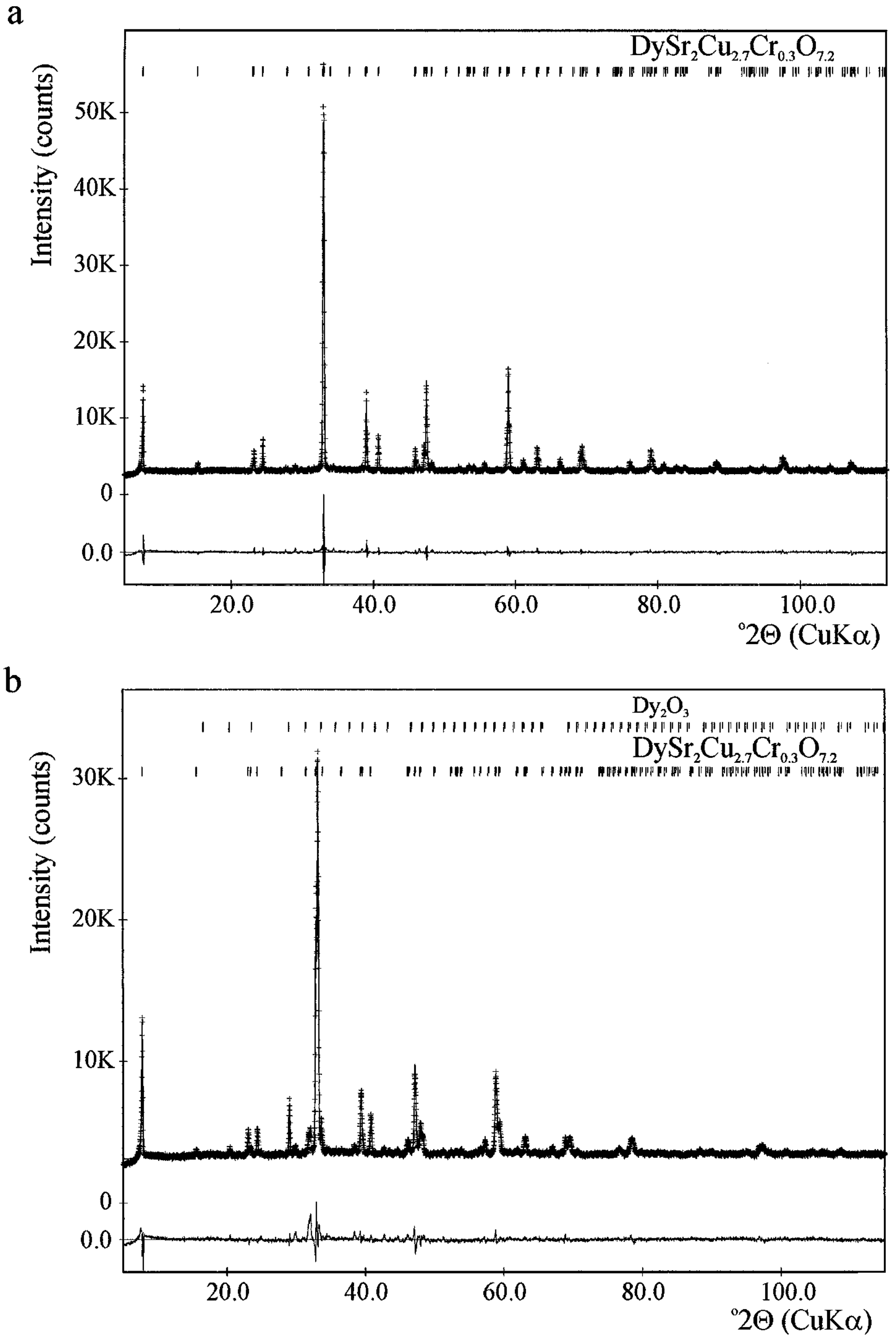

FIG. 1. Observed, calculated, and difference diffraction patterns after structure refinement.

short, especially for the Cr compound. This suggests strong bonding between these atoms.

Despite some differences between the structures of $DySr_2Cu_{2.7}Mo_{0.3}O_{7.2}$ and $DySr_2Cu_{2.7}Cr_{0.3}O_{7.2}$, the positions of the heavy atoms are typical for 123-type oxides (and very similar to those in the Ho phase). The greatest difference is in the location of chromium and molybdenum. The first substitutes for copper in the 00*z* position whereas the second substitutes in the 000 position. These positions are often described as "plane" and "chain" positions because of the characteristic structure of layers formed by copper and oxygen in the YBCO 123 phases. The thickness of the plane layers may be estimated by the distances between the Sr and Dy atoms along the *z* axis whereas the thickness of the chain

TABLE 3
Atomic Positional and Thermal Parameters for $DySr_2Cu_{2.7}Mo_{0.3}O_{7.2}$

Atom	Wyckoff site	x	y	z	B	Occupancy[a]
Dy	1d	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	0.27(9)	
Sr	2h	$\frac{1}{2}$	$\frac{1}{2}$	0.1958(2)	0.6(1)	
Cu/Mo [Cu(1)]	1a	0	0	0	2.7(2)	0.55/0.45(2)
Cu [Cu(2)]	2g	0	0	0.3547(5)	0.68(8)	
O [O(1)]	4n	0.210(9)	$\frac{1}{2}$	0	3(2)	0.36(2)
O [O(2)]	4i	0	$\frac{1}{2}$	0.3720(8)	0.2(3)	
O [O(3)]	2g	0	0	0.158(2)	1.4(4)	

[a] Equal to 1 if not specified.

TABLE 4
Atomic Positional and Thermal Parameters for $DySr_2Cu_{2.7}Cr_{0.3}O_{7.2}$

Atom	Wyckoff site	x	y	z	B	Occupancy[a]
Dy	1d	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	1.8(2)	
Sr	2h	$\frac{1}{2}$	$\frac{1}{2}$	0.1914(4)	2.8(2)	
Cu [Cu(1)]	1a	0	0	0	2.2(2)	
Cu/Cr [Cu(2)]	2g	0	0	0.3534(7)	0.1(2)	0.85/0.15
O [O(1)]	4n	0.18(1)	$\frac{1}{2}$	0	3(2)	0.35(2)
O [O(2)]	4i	0	$\frac{1}{2}$	0.366(2)	1.9(6)	
O [O(3)]	2g	0	0	0.153(4)	2.8(6)	

[a] Equal to 1 if not specified.

layers may be estimated by the distance of Sr atoms measured along the z axis in two adjacent unit cells. The thickness of the plane layer is almost the same for the Mo and Cr compounds, respectively equal to 3.513(5) and 3.512(3) Å. The thickness of the chain layer is different in the compounds (4.523(4) and 4.356(7) Å for the Mo and Cr compounds, respectively), which results in a different length of the c period. This shows that the substitution of copper in the chain layer leads to larger changes than its analogous substitution in the plane layer. These changes refer to the thickness of layers and to the shift of the O(1) position. The substitution of copper in the 000 position (Mo case) results in a larger shift of oxygen O(1) than if it were substituted in the 00z position.

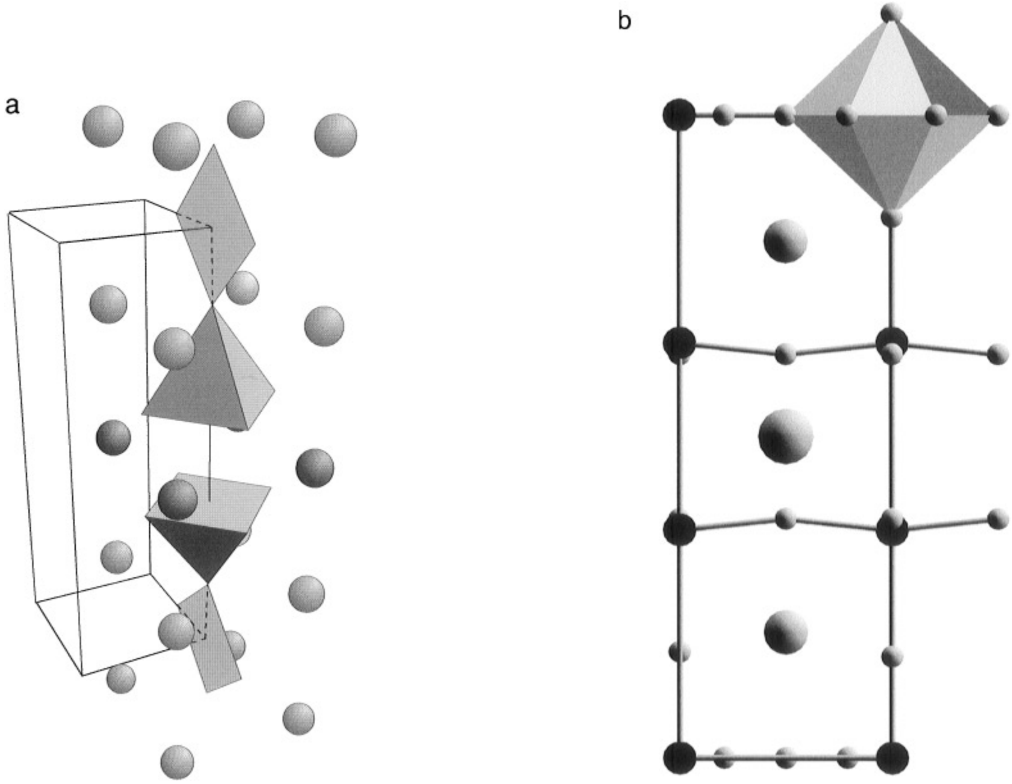

FIG. 2. Partial representations of the structures of $YBa_2Cu_3O_7$ (a) and $DySr_2Cu_{2.7}Mo_{6.3}O_{7.2}$ (b) along the b axis. In (a) atoms of oxygen are shown as vertices of coordination polyhedra of copper and in (b) as small balls.

TABLE 5
Selected Bond Distances (Å) and Angles (Deg) for $DySr_2Cu_{2.7}Mo_{0.3}O_{7.2}$

Dy–O(2) ×8	2.418(6)	Sr–O(1)[a] ×4	2.52(2)
Sr–O(2) ×4	2.793(7)	Sr–O(3) ×4	2.740(4)
Cu(1)–O(1)[a] ×2	2.08(2)	Cu(1)–O(3) ×2	1.83(3)
Cu(2)–O(2) ×4	1.923(2)	Cu(2)–O(3) ×1	2.27(3)
Dy–Sr ×2	3.513(5)	O(1)–O(1)[a] ×2	1.57(4)
Sr–Sr ×1	4.523(4)		
O(2)–Cu(2)–O(2)	168.1(6)	O(2)–Cu(2)–O(2)	89.38(6)
O(2)–Cu(2)–O(3)	96.0(3)	Cu(1)–O(1)–Cu(1)	134(2)
Cu(2)–O(2)–Cu(2)	168.1(6)	Cu(1)–O(3)–Cu(2)	180

[a] The O(1) species is partially occupied (Table 3).

TABLE 6
Selected Bond Distances (Å) and Angles (Deg) for $DySr_2Cu_{2.7}Cr_{0.3}O_{7.2}$

Dy–O(2) ×8	2.45(2)	Sr–O(1)[a] ×4	2.51(2)
Sr–O(2) ×4	2.77(2)	Sr–O(3) ×4	2.760(8)
Cu(1)–O(1)[a] ×2	2.04(2)	Cu(1)–O(3) ×2	1.74(5)
Cu(2)–O(2) ×4	1.932(2)	Cu(2)–O(3) ×1	2.28(5)
Dy–Sr ×2	3.512(5)	O(1)–O(1)[a] ×2	1.36(6)
Sr–Sr ×1	4.356(7)		
O(2)–Cu(2)–O(2)	171(2)	O(2)–Cu(2)–O(2)	89.67(9)
O(2)–Cu(2)–O(3)	94.4(8)	Cu(1)–O(1)–Cu(1)	141(3)
Cu(2)–O(2)–Cu(2)	171(2)	Cu(1)–O(3)–Cu(2)	180

[a] The O(1) species is partially occupied (Table 4).

CONCLUSIONS

We have found that the substitution of Cu by molybdenum enables formation of the $DySr_2Cu_{2.7}Mo_{0.3}O_x$ monopahse at 950°C. In the case of $DySr_2Cu_{2.7}Cr_{0.3}O_x$, the synthesis carried out under the same conditions led to a product containing the impurities Dy_2O_3 and $Sr_{14-y}Dy_yCu_{24}O_x$. This suggests that the latter phase is a precursor in the process of $DySr_2Cu_{2.7}Cr_{0.3}O_x$ formation and shows the similarities in the formation of $DySr_2Cu_{2.7}Cr_{0.3}O_x$ and $YSr_2Cu_{3-y}Mo_yO_x$, for which Wu (13) has found that $Sr_{14-y}Y_yCu_{24}O_{41}$ is a precursor.

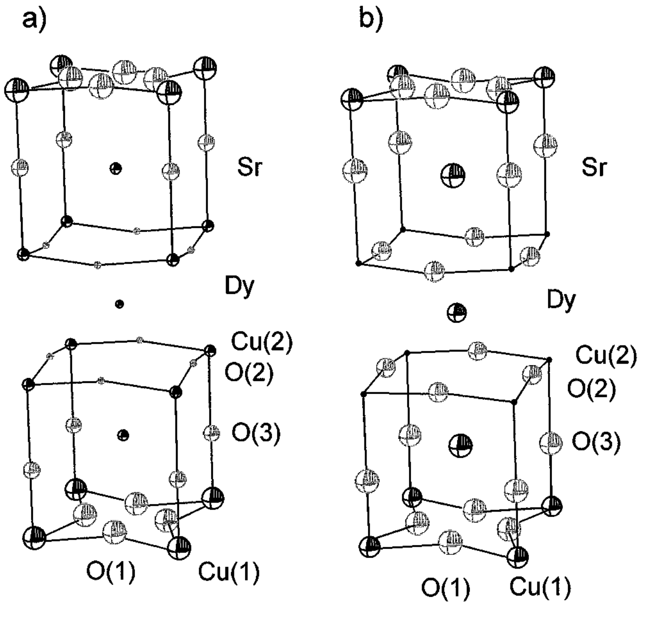

FIG. 3. Projections of the structures of $DySr_2Cu_{2.7}Mo_{0.3}O_{7.2}$ (a) and $DySr_2Cu_{2.7}Cr_{0.3}O_{7.2}$ (b) along the *a* axis.

The structures of both phases have been refined using the Rietveld method. It was found that the substitution of copper in the 000 position affects the geometry of the structure much more strongly than substitution in the 00*z* position.

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