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Short Communication

Superconducting Cuprates and Related Oxides, VIII. Composition and Structure of the Single Crystals $La_{1.89}Sr_{0.11}CuO_4$ and $Nd_{1.81}Ce_{0.19}CuO_4$

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The hole-doped superconductor system $La_{2-x}Sr_xCuO_4$ and the electron-doped superconductor system $Nd_{2-x}Ce_xCuO_4$ have been intensively studied by several research groups. In the present communication single-crystal neutron diffraction analysis has been used to test if this method could be used to determine a deviation from stoichiometry of the copper atoms in $La_{2-x}Sr_xCuO_4$ and in $Nd_{2-x}Ce_xCuO_4$. Such a deviation from stoichiometry has been reported.[1]

The $La_{2-x}Sr_xCuO_4$ and $Nd_{2-x}Ce_xCuO_4$ single crystals were obtained by a temperature gradient technique,[1] which makes it possible to grow crystals at a very low supercooling (less than the metastable zone width 2 K in these systems). At such temperature gradients the natural convective mass transfer is small and is amplified by stirring the solution in rotating the crucible. This method yields crystals with volumes up to 0.2–0.3 cm^3. For the La–Sr–Cu–O system the starting composition was $La_2O_3:SrO:CuO = 2:0.8:16$ mol and the growth temperature was 1070 °C. For the Nd–Ce–Cu–O system the starting composition was $Nd_2O_3:CeO_2:CuO = 2:0.2:18$ mol and the growth temperature was 1150 °C. Pt crucibles were used in both cases. Analyses of the crystals were performed by using the EPMA technique which gave the following compositions: $La_{1.89}Sr_{0.11}Cu_{0.92}Pt_{0.01}O_4$ and $Nd_{1.81}Ce_{0.19}Cu_{0.91}Pt_{0.02}O_4$. The standard deviation of the EPMA analysis is typically 0.01. Both crystals were non-superconductors because the Cu deficiency was higher than 0.04 at./f.u. for the lanthanum cuprate single crystal, and the Pt content was 0.02 at./f.u. for the neodymium cuprate single crystal. The dependence of the Cu deficiency in $La_{2-x}Sr_xCu_{1-y}O_{4-d}$ single crystals versus growth conditions and how it affects superconducting properties was discussed in Ref. 1 in detail. The role of growth conditions for the composition and superconducting properties of $Nd_{2-x}Ce_xCuO_{4-d}$ single crystals will be published elsewhere.

The crystal structure of $La_{1.89}Sr_{0.11}CuO_4$ is similar to that of $La_{1.85}Sr_{0.15}CuO_4$,[2] and the crystal structure of $Nd_{1.81}Ce_{0.19}CuO_4$ is similar to that of Nd_2CuO_4.[3] The neutron diffraction data were measured on a Huber four-circle diffractometer at DR3, Risø National Laboratory. Experimental conditions are listed in Table 1. The reflections were measured in a sphere with the Miller indices limits $-5 \leqslant h$ and $k \leqslant 5$, $-17 \leqslant l \leqslant 17$. Absorption correction of the data was made by Gaussian integration.

The models of the structures were refined using the least-squares program LINUS,[4] and the atomic scattering lengths La: 0.824, Sr: 0.702, Nd: 0.769, Ce: 0.484, Cu: 0.7718, Pt: 0.960, O: 0.5805, all in the units (10^{-12} cm).[5] Starting values of the positional parameters of the atoms were taken from Refs. 2 and 3, respectively. The final positional and thermal parameters are listed in Table 2.

Two models were tested for the $La_{2-x}Sr_xCuO_4$ crystal, a model with a Cu-nonstoichometry and the composition $La_{1.89}Sr_{0.11}Cu_{0.92}Pt_{0.01}O_4$ and a stoichiometric model with the composition $La_{1.89}Sr_{0.11}CuO_4$. The higher R-value was found for the composition that was nonstoichiometric with respect to Cu. However, the refined parameters for the two models were not significantly different

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Table 1. Experimental data and unit-cell parameters for the investigated single crystals.

	$La_{1.89}Sr_{0.11}CuO_4$	$Nd_{1.81}Ce_{0.19}CuO_4$
Unit cell parameters:		
a/Å	3.785(2)	3.948(4)
b/Å	3.785(2)	3.948(4)
c/Å	13.201(8)	12.033(9)
Cell volume/Å^3	189.13	187.55
Space group	*I*4/*mmm*	*I*4/*mmm*
Z	2	2
Size of crystal/mm	3.55 × 5.15 × 2.90	2.60 × 4.60 × 1.85
Density (calc.)/g cm^{-3}	7.01	7.36
Linear absorption coefficient, μ/cm^{-1}	0.13	0.56
Min. and max. transmission	0.95–0.97	0.86–0.91
Wavelength of neutrons/Å	1.047	1.047
No. of measured reflections	658	653
R(intern.) of reflections (%)	2.4	2.2
No of reflections with $I>3\sigma(I)$	120	117
Scan method	$\omega-2\theta$	$\omega-2\theta$

Table 2. Atomic coordinates and temperature factor parameters ($\times 10^4$).

Atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{11}	U_{22}	U_{33}
Composition: $La_{1.89}Sr_{0.11}Cu_{0.92}Pt_{0.01}O_4$, *R*=2.6%, [$La_{1.89}Sr_{0.11}Cu_{1.00}O_4$], *R*=2.1%.						
La (Sr)	0	0	0.36088(8)	114(7)	114(7)	5(1)
			[0.36089(6)	107(5)	107(5)	5(1)]
Cu	0	0	0	21(8)	21(8)	9(1)
				[45(6)	45(6)	11(1)]
O1	0	1/2	0	119(11)	67(11)	19(1)
				[113(8)	64(8)	18(1)]
O2	0	0	0.18236(13)	309(10)	309(10)	11(1)
			[0.18238(10)	302(8)	302(8)	10(1)]
Isotropic extinction parameter				0.206(16)		
				[0.199(12)]		
Composition: $Nd_{1.81}Ce_{0.19}Cu_{0.91}Pt_{0.02}O_4$, *R*=2.2%, [$Nd_{1.81}Ce_{0.19}Cu_{1.00}O_4$], *R*=2.2%.						
Nd (Ce)	0	0	0.35271(12)	77(6)	77(6)	7(1)
			[0.35265(13)	63(7)	63(7)	6(1)]
Cu	0	0	0	62(8)	62(8)	8(1)
				[81(9)	81(9)	12(1)]
O1	0	1/2	0	154(12)	108(12)	17(1)
				[151(13)	108(13)	15(1)]
O2	0	1/2	1/4	103(8)	103(8)	14(1)
				[103(9)	103(9)	12(1)]
Isotropic extinction parameter				0.061(9)		
				[0.051(9)]		

from each other. The temperature factor parameters for Cu are lower in the nonstoichiometric model, which is in favour of that model. However, the nonstoichiometric model has a higher *R*-value. The single-crystal neutron diffraction analysis thus gives no clear answer to the question of Cu nonstoichiometry in the crystal.

Two models were tested for the $Nd_{2-x}Ce_xCuO_4$ crystal, a model with a Cu nonstoichiometry and the composition $Nd_{1.81}Ce_{0.19}Cu_{0.91}Pt_{0.02}O_4$ and a stoichiometric model with the composition $Nd_{1.81}Ce_{0.19}CuO_4$. The *R*-values for the two models are identical, and the refined parameters do not deviate significantly from each other for the two models. The temperature factor parameters for Cu are lower in the nonstoichiometric model, which is in favour of that model. In this case also, the single-crystal neutron diffraction analysis does not give a clear answer to the question of the Cu nonstoichiometry in the crystal. However, the microprobe analysis displays a tendency towards Cu nonstoichiometry for the crystals investigated.

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