

## Superconducting Cuprates and Related Oxides. III. Crystal Structure of $\text{NdSrBaCu}_{2.88}\text{O}_{6.8}$ and of $\text{Nd}_{1.33}\text{Ca}_{0.25}\text{Ba}_{1.42}\text{Cu}_{2.92}\text{O}_{6.8}$

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The metal atoms yttrium, barium and copper on the metal sites of the crystal structure of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  can be substituted by other metal atoms.<sup>1-7</sup> Compounds of the type  $\text{RECaBaCu}_3\text{O}_{7-\delta}$  and  $\text{RESrBaCu}_3\text{O}_{7-\delta}$  (RE = La, Nd and Ho) were recently characterized by X-ray as well as by neutron diffraction powder methods, and profile refinements were made with models of the structure using the space groups  $P4/mmm$  (No. 123) and  $Pmmm$  (No. 47).

The effective ionic radii [ $\text{La}^{3+}$ , 1.18;  $\text{Nd}^{3+}$ , 1.12;  $\text{Ca}^{2+}$ , 1.12;  $\text{Sr}^{2+}$ , 1.25 and  $\text{Ba}^{2+}$ , 1.42 Å (eight coordination)]<sup>8</sup> do suggest a stronger tendency for Ca than for Ba and Sr for substitution on the RE sites. In Ref. 5 it was found for  $\text{LaCaBaCu}_3\text{O}_{7-\delta}$  and  $\text{LaSrBaCu}_3\text{O}_{7-\delta}$  that  $\text{Sr}^{2+}$  ions enter at the  $\text{Ba}^{2+}$  sites in preference to the  $\text{La}^{3+}$  sites, and  $\text{Ca}^{2+}$  ions enter at the  $\text{La}^{3+}$  sites in preference to the  $\text{Ba}^{2+}$  sites. In this substitution the solid solutions have the chemical composi-

tions  $\text{La}_{1.23}\text{Ca}_{0.54}\text{Ba}_{1.23}\text{Cu}_3\text{O}_{7-\delta}$  and  $\text{La}_{1.14}\text{Sr}_{0.72}\text{Ba}_{1.14}\text{Cu}_3\text{O}_{7-\delta}$ , and have the respective crystallographic compositions  $(\text{La}_{0.59}\text{Ca}_{0.41})(\text{Ba}_{1.23}\text{Ca}_{0.13}\text{La}_{0.64})\text{Cu}_3\text{O}_{7-\delta}$  and  $(\text{La}_{0.93}\text{Sr}_{0.07})(\text{Ba}_{1.14}\text{Sr}_{0.65}\text{La}_{0.21})\text{Cu}_3\text{O}_{7-\delta}$ .<sup>5</sup>

Such a distribution of atoms on the different crystallographic sites could not be confirmed in profile refinements of the models of the structures of  $\text{HoSrBaCu}_3\text{O}_{7-\delta}$ ,  $\text{NdSrBaCu}_3\text{O}_{7-\delta}$ ,  $\text{LaSrBaCu}_3\text{O}_{7-\delta}$ ,  $\text{NdCaBaCu}_3\text{O}_{7-\delta}$  and  $\text{LaCaBaCu}_3\text{O}_{7-\delta}$ , using X-ray or neutron diffraction powder patterns.<sup>6,7</sup> This could possibly be due to the powder diffraction patterns having a resolution that was too low and a  $2\theta$  range that was too narrow. For this reason it was decided to repeat the investigation of the structures of  $\text{NdSrBaCu}_3\text{O}_{7-\delta}$  and  $\text{NdCaBaCu}_3\text{O}_{7-\delta}$  using high-resolution synchrotron X-ray radiation out to  $\sin \theta/\lambda = 0.585$ . A similar investigation of  $\text{HoBa}_2\text{Cu}_3\text{O}_{7-\delta}$  was also performed.

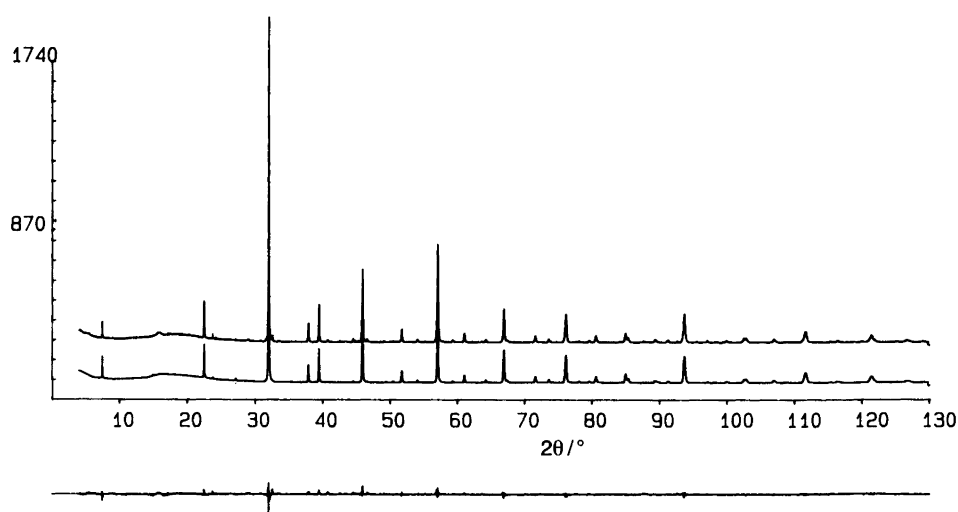


Fig. 1. Powder pattern of  $\text{NdSrBaCu}_{2.88}\text{O}_{6.8}$ . The upper and lower curves represent the observed and calculated profiles, respectively with the difference shown in the lower part of the figure.

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The samples were the same as used in the previous investigations.<sup>6,7</sup> Prior to the measurements the samples were annealed in oxygen at 950 °C for 24 h, at 550 °C for 24 h, at 400 °C for 12 h and then cooled to room temperature over 5 h.

The synchrotron X-ray powder patterns were measured on the high-resolution powder diffractometer on Station 8.3 at Daresbury, UK<sup>9</sup> using a wavelength of 1.5405 Å. A flat-plate diffraction geometry was used, and the samples were rotated to obtain maximum randomization of the crystal grains. The diffraction patterns were measured in 2θ steps of 0.01° in the 2θ interval 4.0–130.0°. In the least-squares profile refinements of the structure as two programs were used: EDINP,<sup>10</sup> with scattering contributions from neutral metal atoms,<sup>11</sup> and DBW3.2S, with built-in scattering contributions.<sup>12</sup>

*NdSrBaCu<sub>2.88</sub>O<sub>6.8</sub>*. The powder pattern (Fig. 1) showed no splitting of Bragg reflections, which would normally indicate an orthorhombic unit cell. The space group *P4/mmm* (No. 123) was assumed, and the starting parameters for the refinement of the model were taken from Ref. 6. A model assuming the crystallographic composition (Nd<sub>1.00-α</sub>Sr<sub>α</sub>)-(Ba<sub>1.00</sub>Sr<sub>1.00-α</sub>Nd<sub>α</sub>)Cu<sub>3.00-β</sub>O<sub>7-δ</sub> was used. In the preparation of the sample a Nd:Ba:Sr ratio of 1:1:1 was applied, and the diffraction pattern of the sample had no reflections of unidentified phases. The best agreement between observed and calculated powder pattern (Fig. 1) was obtained for α = 0.28, β = 0.12 and δ = 0.2. The values for the refined parameters are listed in Table 1. For definition of the profile parameters and the *R*-values see Refs. 6 and 7. The investigation thus confirms that Sr<sup>2+</sup> ions enter the Ba<sup>2+</sup> site in preference to the Nd<sup>3+</sup> site, in analogy to the results

**Table 1.** Structure parameters for NdSrBaCu<sub>2.88</sub>O<sub>6.8</sub>; tetragonal space group *P4/mmm* (No. 123); powder pattern measured at 30 K; composition from crystallographic analysis: (Nd<sub>0.72</sub>Sr<sub>0.28</sub>)(Ba<sub>1.00</sub>Sr<sub>0.72</sub>Nd<sub>0.28</sub>)Cu<sub>2.88</sub>O<sub>6.8</sub>.<sup>a</sup>

Atom	Site	A <sup>b</sup>	x/a	y/b	z/c	B/Å <sup>2</sup>
Nd	1d	0.72(2)	1/2	1/2	1/2	0.0(1)
Sr	1d	0.28(2)				
Ba	2h	1.00				
Sr	2h	0.72(2)				
Nd	2h	0.28(2)	1/2	1/2	0.176(1)	1.2(1)
Cu1	1a	0.88(2)				
Cu2	2g	2.00				
O1	2g	2.00				
O2	4i	4.00	0	1/2	0.355(2)	1.4(1)
O3	2f	0.8(1)	0	1/2	0	1.2(1)

<sup>a</sup>Profile parameters, unit cell parameters and *R*-values were obtained from the program EDINP. *U* = 0.057(1), *V* = -0.004(1), *W* = -0.001(1) and *T* = 0.046(1); *a* = 3.8579(1) and *c* = 11.5952(2) Å; *R<sub>E</sub>* = 5.9%, *R<sub>P</sub>* = 5.9%, *R<sub>wp</sub>* = 7.9%, *R<sub>F</sub>* = 9.3% and *R<sub>I</sub>* = 9.1%. <sup>b</sup>*A* is the Wyckoff number multiplied by the occupancy.

**Table 2.** Structure parameters for Nd<sub>1.33</sub>Ca<sub>0.25</sub>Ba<sub>1.42</sub>Cu<sub>2.92</sub>O<sub>6.8</sub>; tetragonal space group *P4/mmm* (No. 123); powder pattern measured at 35 K; composition from crystallographic analysis: (Nd<sub>0.78</sub>Ca<sub>0.22</sub>)(Ba<sub>1.42</sub>Ca<sub>0.03</sub>Nd<sub>0.55</sub>)Cu<sub>2.92</sub>O<sub>6.8</sub>.<sup>a</sup>

Atom	Site	A <sup>b</sup>	x/a	y/b	z/c	B/Å <sup>2</sup>
Nd	1d	0.78(2)	1/2	1/2	1/2	1.2(1)
Ca	1d	0.22(2)				
Ba	2h	1.42(2)				
Ca	2h	0.03(2)	1/2	1/2	0.183(1)	1.3(1)
Nd	2h	0.55(2)				
Cu1	1a	0.92(2)	0	0	0	2.3(1)
Cu2	2g	2.00	0	0	0.353(1)	1.5(1)
O1	2g	2.00	0	0	0.177(1)	2.7(1)
O2	4i	4.00	0	1/2	0.372(2)	2.3(1)
O3	2f	0.8(1)	0	1/2	0	2.3(1)

<sup>a</sup>Profile parameters, unit cell parameters and *R*-values were obtained from the program EDINP. *U* = 0.077(1), *V* = -0.000(1), *W* = 0.004(1) and *T* = 0.103(1); *a* = 3.8639(2) and *c* = 11.6009(5) Å; *R<sub>E</sub>* = 5.7%, *R<sub>P</sub>* = 7.7%, *R<sub>wp</sub>* = 10.3%, *R<sub>F</sub>* = 18.3% and *R<sub>I</sub>* = 13.8%. <sup>b</sup>See Table 1.

**Table 3.** Structure parameters for HoBa<sub>2</sub>Cu<sub>2.90</sub>O<sub>6.85</sub>; orthorhombic space group *Pmmm* (No. 47); powder pattern measured at 30 K; composition from crystallographic analysis: HoBa<sub>2</sub>Cu<sub>2.90</sub>O<sub>6.85</sub>.<sup>a</sup>

Atom	Site	A <sup>b</sup>	x/a	y/b	z/c	B/Å <sup>2</sup>
Ho	1h	1	1/2	1/2	1/2	0.8(2)
Ba	2t	2	1/2	1/2	0.1817(3)	0.9(2)
Cu1	1a	0.90(2)	0	0	0	1.2(2)
Cu2	2q	2	0	0	0.347(7)	0.4(2)
O1	2q	2	0	0	0.143(3)	2.0(2)
O2	2s	2	1/2	0	0.379(3)	0.5(2)
O3	2r	2	0	1/2	0.407(3)	0.5(2)
O4	1e	0.85(2)	0	1/2	0	2.0(2)

<sup>a</sup>Profile parameters, preferred orientation parameters, unit cell parameters, and *R*-values from program DBW3.2S. *U* = 0.084(5), *V* = -0.002(3), *W* = 0.002(1), *NA* = 1.21(3), *NB* = -0.001(1), *G<sub>1</sub>* = -1.13(10) and *G<sub>2</sub>* = 0.51(2); *a* = 3.8273(1), *b* = 3.8763(2) and *c* = 11.6281(7) Å; *R<sub>E</sub>* = 5.6%, *R<sub>P</sub>* = 8.8%, *R<sub>wp</sub>* = 12.2% and *R<sub>I</sub>* = 20.6%. <sup>b</sup>See Table 1.

reported by Fujishita *et al.*<sup>4</sup> In addition, the Cu1 atom at site 1a shows non-stoichiometry.

*Nd<sub>1.33</sub>Ca<sub>0.25</sub>Ba<sub>1.42</sub>Cu<sub>2.92</sub>O<sub>6.8</sub>*. The synchrotron X-ray powder pattern for this compound also indicated a tetragonal unit cell. In the sample preparation a Nd:Ca:Ba ratio of 1:1:1 was applied, but the sample contained an impurity of Ca<sub>2</sub>CuO<sub>3</sub>. In the model calculations the following crystallographic composition was assumed: (Nd<sub>1.00-α</sub>Ca<sub>α</sub>)-(Ba<sub>2.00-ε-γ</sub>Ca<sub>ε</sub>Nd<sub>γ</sub>)Cu<sub>3.00-β</sub>O<sub>7-δ</sub>. The best agreement between observed and calculated powder patterns was observed for α = 0.22, γ = 0.55, ε = 0.03, β = 0.08 and δ = 0.2. The refined parameters are listed in Table 2. The Ca<sup>2+</sup> ions

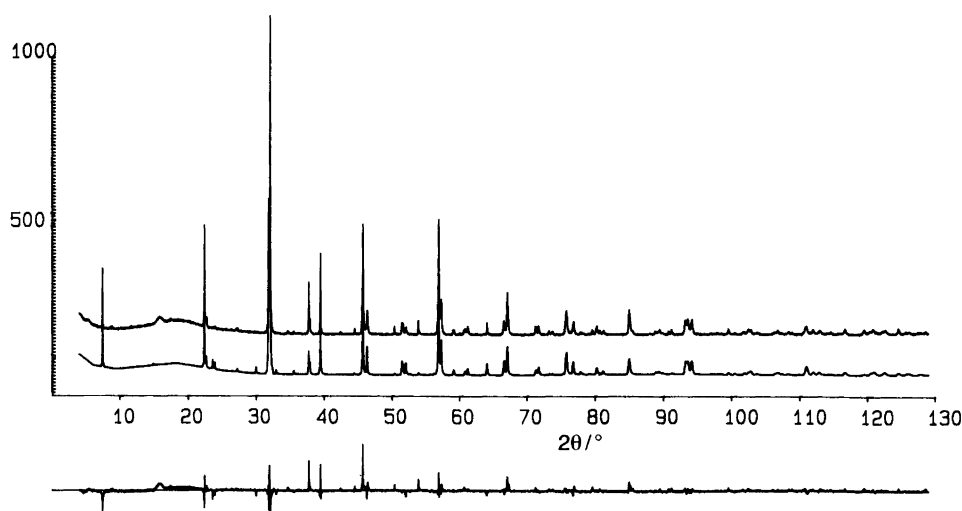


Fig. 2. Powder pattern of  $\text{HoBa}_2\text{Cu}_{2.90}\text{O}_{6.85}$ . The upper and lower curves represent the observed and calculated profiles, respectively. The difference between the two curves is shown in the lower part of the figure. The sample showed a slight tendency to a preferred orientation after (001).

have a tendency to enter the  $\text{Nd}^{3+}$  site in preference to the  $\text{Ba}^{2+}$  site. For this compound also, the Cu1 atom at site 1a shows non-stoichiometry.

$\text{HoBa}_2\text{Cu}_{2.90}\text{O}_{6.85}$ . The sample was superconducting at 90 K, and the powder pattern (Fig. 2) indicates an orthorhombic unit cell (Table 3). The starting parameters for refinement of the model of the structure were taken from Ref. 13, and the values of the refined parameters are listed in Table 3. This compound also shows non-stoichiometry for the Cu1 atom at site 1a.

In refinement of the occupancy of site 1a all three structures show a copper non-stoichiometry for Cu1. Such a copper non-stoichiometry has also been found in the profile refinement of the X-ray powder pattern of  $\text{LaBa}_2\text{Cu}_{2.88}\text{O}_{6.8}$ ,<sup>14</sup> in single-crystal X-ray diffraction analysis of  $\text{YBa}_2\text{Cu}_{2.91}\text{O}_{6.4}$ <sup>15</sup> and in the profile refinement of the neutron diffraction powder pattern of  $\text{YBa}_2\text{Cu}_{2.96}\text{O}_6$ .<sup>13</sup>

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