Short Communication

Crystal Structure of $Y_2(Ba,Sr)_2SrPtCu_2O_{10}$

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Since the discovery of superconductivity in certain metal oxides[1-3] with structures containing perovskite layers, such as e.g. $YBa_2Cu_3O_{7-x}$, interest in metal oxides has increased dramatically. Studies of such metal oxides with numerous different metal ions have been undertaken in order to discover new superconducting phases.

Phases containing platinum can be obtained as unwanted by-products from solid state syntheses in platinum crucibles. Recent investigations have shown the existence of phases such as $Y_2Ba_2PtCuO_8$[4-6] and $Y_2Ba_3PtCu_2O_{10}$[7] in oxide systems of this type. In the present study a crystalline phase was observed near the wall of the platinum crucible when attempting to prepare $Y(Ba,Sr)_2Cu_3O_{7-x}$. A structural investigation of selected crystals from this phase indicated the composition to be $Y_2Ba_{1.25}Sr_{1.75}PtCu_2O_{10}$. Despite the large difference in chemical composition the results show that the structure found is isotypic with that of $Y_2Ba_3PtCu_2O_{10}$. In view of the great interest of the different phases occurring in oxide systems containing superconducting specimens it was considered worthwhile to perform a complete structure determination of the present phase, thus contributing to our knowledge concerning oxides of this type. The present study also shows how a large fraction of the barium ions in $Y_2Ba_3PtCu_2O_{10}$ can be substituted by strontium ions while maintaining the general features of the structure.

Experimental

Single crystals of $Y_2(Ba,Sr)_2SrPtCu_2O_{10}$ were obtained by heating a micture of Y_2O_3, $BaCO_3$, $SrCO_3$ and CuO (molar ratio 1:2:2:6) in a platinum crucible at 1200 °C for three days. The crystals mainly appeared at the wall of the crucible.

Single-crystal X-ray diffraction data were collected for a selected crystal with an Enraf-Nonius CAD4 diffractometer, and were corrected for background, Lorentz, polarization and absorption effects. The crystal dimensions used for the absorption correction were verified by analysis of the intensity distributions obtained by psi-scans of 10 different reflections. A summary of the experimental conditions is given in Table 1.

Systematic absences indicated a symmetry in accordance with the C-centered space groups C2, Cm or C2/m. The centrosymmetric space group C2/m chosen was supported by the outcome of the structural refinements.

The structure was solved by heavy-atom techniques using the SHELX76[7] program package. The final refinements with anisotropic thermal parameters for all atoms were carried out with the least-squares program UPALS[9] which *inter alia* allows refinement of extinction parameters in the Becker and Coppens formalism.[10] Refinement of the isotropic type I extinction parameter showed no significant extinction effects, and this parameter was omitted in the final refinement. Scattering factors for neutral atoms were taken from Ref. 11,[11] and the final atomic coordinates and isotropic thermal parameters are listed in Table 2. Listings of observed and calculated structure factors as well as anisotropic temperature factors are available from the author on request.

Table 1. Experimental conditions for the crystal structure determination of $Y_2(Ba,Sr)_2SrPtCu_2O_{10}$.

Formula	$Y_2Ba_{1.25(2)}Sr_{1.75(2)}PtCu_2O_{10}$
Formula weight	985.0
Space group	$C2/m$
Unit cell/Å	$a = 12.316(2)$, $b = 5.707(2)$, $c = 7.323(1)$
Unit cell/°	$\beta = 105.53(1)$
Unit cell volume/Å^3	497.7(1)
Formula units per unit cell	2
Calculated density/g cm^{-3}	6.573(1)
Radiation	MoKα
Wavelength/Å	0.71073
Temperature/K	293(1)
Crystal size/mm	$0.025 \times 0.085 \times 0.025$
Diffractometer	Enraf-Nonius CAD4
Determination of unit cell:	
Number of reflections used	16
θ-range/°	7.14 to 15.3
Intensity data collection:	
Maximum $\sin(\theta)/\lambda/Å^{-1}$	1.20
Range of h, k and l	−29 to 28, 0 to 13 and 0 to 17
Standard reflections	(0 2 0), (3 −3 1) and (0 4 0)
Intensity instability	negligible
Number of collected refl.	4009
Number of unique refl.	3949
Number of observed refl.	2063
Criterion for significance	$I > 5\ \sigma(I)$
Absorption correction:	
Linear absorption coefficient/cm^{-1}	430.8
Transmission factor range	0.02 to 0.28
Structure refinement:	
Minimization of	Sum of $w(\Delta F)^2$
Number of refined parameters	52
Weighting scheme	$(\sigma_F^2 + 0.0001 \cdot F^2)^{-1}$
$R = \Sigma(F_o - F_c)/\Sigma F_c$	0.0397
$R_w = (\Sigma w(F_o)^2/\Sigma wF_c^2)^{\frac{1}{2}}$	0.0458

Discussion

As mentioned above, the structure of the present compound is isotypic with that of $Y_2Ba_3PtCu_2O_{10}$.[7] Thus, the structure can be described by means of the different oxygen coordination polyhedra observed around the metal atoms. The coordination polyhedra around Y^{3+} and Cu^{2+} are similar to those observed for the Y_2BaCuO_5 type structure (see e.g. Michel and Raveau[13]), and the coordination of copper is such that four shorter (1.920–2.059 Å) and one longer (2.427 Å) Cu-O bonds are found. The octahedral coordination of Pt is in agreement with what is generally observed in Pt^{4+} compounds, and the Pt-O distances, ranging from 2.014 to 2.025 Å, are equal within three e.s.d's. The bond distances

in the coordination polyhedra are listed in Table 3. The projection of the structure on the (0 1 0) plane is seen in Fig. 1.

The strontium ions of the present compound fully occupy one of the barium sites (8-coordinated) in the $Y_2Ba_3PtCu_2O_{10}$ structure and partially occupy [38(1) %] the other one (11-coordinated). The preference of the strontium ions for occupying the 8-coordinated barium position rather than the 11-coordinated one is clearly due to the smaller size of the strontium ions. The substitution of Ba^{2+} with the smaller Sr^{2+} ion also explains the shorter unit cell axes of the present compound.

In order to compare the metal-oxygen bond distance distribution with that observed in other metal oxides, empirical bond-valences have been

Table 2. Fractional coordinates ($\times 10^5$ for non-oxygen atoms; $\times 10^4$ for oxygen atoms) and temperature factors ($\times 10^4$ for non-oxygen atoms; $\times 10^3$ for oxygen atoms) with e.s.d's in parentheses.

Atom	x	y	z	U_{eq}[a]
Pt	0	0	0	84(3)
Sr	50000	0	50000	102(5)
Ba,Sr	35108(4)	0	−2596(10)	164(4)
Y	18973(6)	0	37251(10)	90(4)
Cu	−8868(8)	0	29747(14)	117(5)
O(1)	1680(5)	0	436(9)	19(4)
O(2)	3241(3)	2634(7)	3788(6)	16(4)
O(3)	192(3)	2286(7)	2178(6)	12(4)

$$^a U_{eq} = \frac{1}{6\pi^2} \sum \beta_{ij}\alpha_i\alpha_j$$

estimated. For this purpose the correlation functions and parameters derived by Brown and Altermatt[14] were used.

The empirical bond valences (4.08, 3.02 and 2.06) for Pt^{4+}, Y^{3+} and Sr^{2+} were in agreement with the formal charges, indicating an average bond distribution in agreement with all the structures from which Brown and Altermatt derived their parametrization. For Cu^{2+} the value 1.89 is calculated, indicating an average bond distribution with longer bonds than expected from the results of Brown and Altermatt. This discrepancy may be ascribed to the pyramidal coordination of the copper ions, whereas the parameters of Brown and Altermatt are mainly derived from the more common square-planar coordination. The bond valence at the mixed Ba-Sr position, calculated as the weighted average for Ba and Sr,

was 1.87. The low value in this case is probably due to differences in coordination for the structures from which the bond valence parameters were derived.

Table 3. Bond distances (in Å) of the coordination polyhedra. Numbers before oxygen atoms give multiplicity.

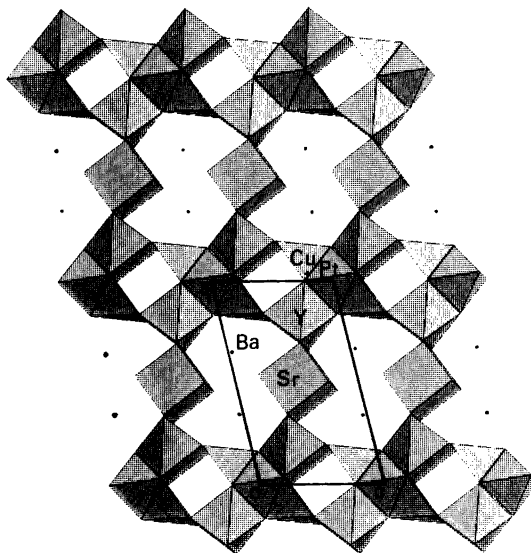|			
Pt−2 O(1)	2.014(6)	Sr−4 O(2)	2.596(4)
Pt−4 O(3)	2.025(4)	Sr−4 O(3)	2.644(4)
Ba(Sr)−O(1)	2.449(6)	Y−2 O(2)	2.231(4)
Ba(Sr)−2 O(3)	2.814(4)	Y−2 O(2)	2.310(4)
Ba(Sr)−2 O(3)	2.855(4)	Y− O(1)	2.351(7)
Ba(Sr)−2 O(1)	2.863(4)	Y−2 O(3)	2.480(4)
Ba(Sr)−2 O(2)	3.193(4)		
Cu−2 O(2)	1.920(4)		
Cu−2 O(3)	2.059(4)		
Cu− O(1)	2.427(7)		

Fig. 1. Polyhedral plot[12] of the structure projected on the (0 1 0) plane, showing the layer at $y = 0$. Stacking of these layers in the b direction, taking into account the vector ($\frac{1}{2}$, $\frac{1}{2}$, 0) due to the C centering, then gives the three-dimensional structure.

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