

BRIEF COMMUNICATION

Structural Refinements of $\text{Yb}_2\text{BaCuO}_5$ and $\text{Lu}_2\text{BaCuO}_5$ by Powder Neutron Diffraction

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Received June 18, 1990; in revised form July 25, 1990

The structures of the "211" or "green phases," $\text{Yb}_2\text{BaCuO}_5$ and $\text{Lu}_2\text{BaCuO}_5$, have been refined from time-of-flight powder neutron diffraction data. Both crystallize in the orthorhombic system, space group $Pnma$, with lattice parameters $a = 12.0588(1) \text{ \AA}$, $b = 5.6123(1) \text{ \AA}$, $c = 7.0535(1) \text{ \AA}$, and $a = 12.0314(1) \text{ \AA}$, $b = 5.5989(1) \text{ \AA}$, $c = 7.0380(1) \text{ \AA}$, respectively. The phases are isostructural with Y_2BaCuO_5 , consisting of a three-dimensional framework of MO_7 units ($M = \text{Yb, Lu}$) enclosing cavities occupied by the Ba and Cu atoms. Ba is 11-coordinate and Cu 5-coordinate, in a distorted square-pyramidal environment.

Introduction

The oxides $M_2\text{BaCuO}_5$ ($M = \text{Y, Sm, Eu, Gd, Dy, Ho, Er, Yb}$) were first reported by Michel *et al.* (1). These authors determined and refined the structure of the $M = \text{Y}$ and Gd phases by a combination of electron microscopy and X-ray powder diffraction. More recently, the structure of the $M = \text{Y}$ phase has been redetermined by single crystal X-ray diffraction (2, 3) and powder neutron diffraction (4, 5). The particular interest in Y_2BaCuO_5 arises from the fact that this phase is often found as an impurity in superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ samples. During our own synthetic studies on the Yb and Lu "123" systems, we have found that the analogous "green phases" also occur here. It is therefore of interest to determine accurately the structural parameters of these phases. In this paper we present detailed structural refinements of $\text{Yb}_2\text{BaCuO}_5$

and $\text{Lu}_2\text{BaCuO}_5$ by powder neutron diffraction.

Experimental

Samples of $\text{Yb}_2\text{BaCuO}_5$ and $\text{Lu}_2\text{BaCuO}_5$ were prepared from oxide precursors BaCO_3 , CuO , and Yb_2O_3 or Lu_2O_3 appropriately mixed to yield the desired metal ion ratios. The powders were mixed thoroughly by grinding, pressed into pellets, and heat treated for 24 hr at 870°C in air. The samples were then reground, passed through a 200 mesh screen, pressed into pellets, and then given a second identical heat treatment.

Powder neutron diffraction data were collected on the Special Environment Powder Diffractometer (6) at Argonne's Intense Pulsed Neutron Source. Data collected in backscattering mode ($2\theta = 150^\circ$) were used for structural refinement by the Rietveld method (7).

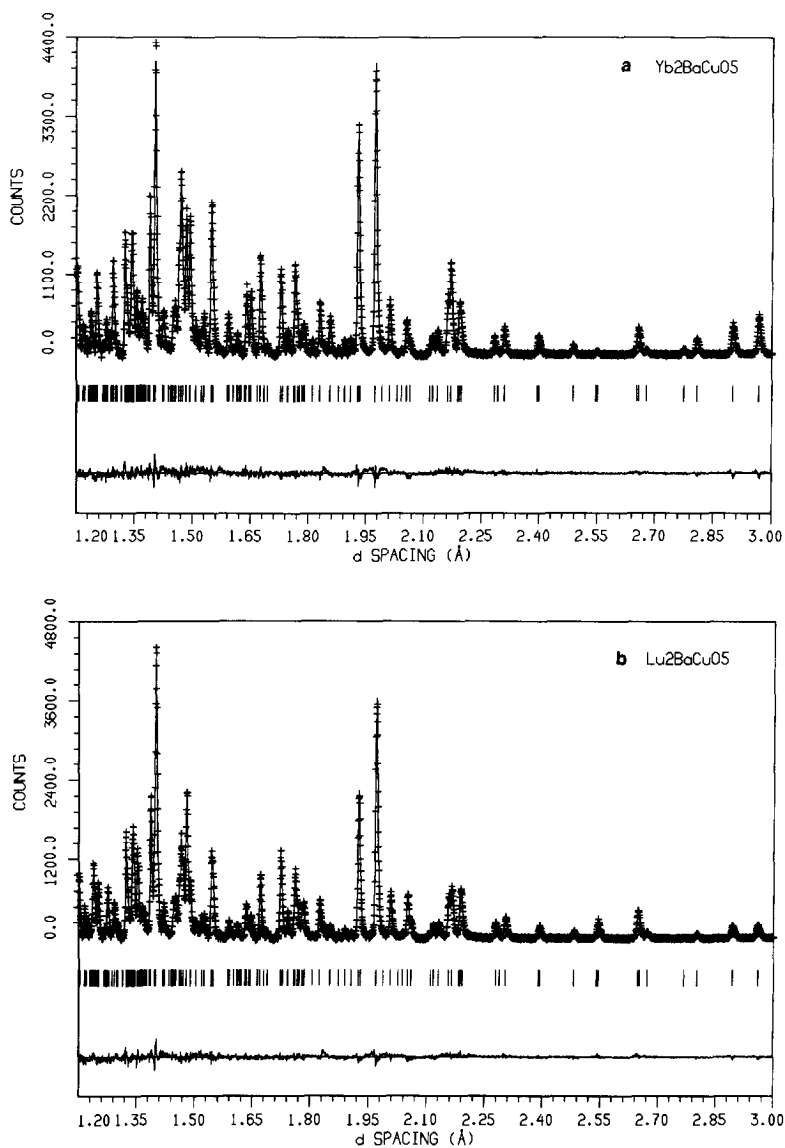


FIG. 1. Portion of the Rietveld refinement profiles for (a) $\text{Yb}_2\text{BaCuO}_5$ and (b) $\text{Lu}_2\text{BaCuO}_5$ at room temperature. Plus marks are the raw data. The solid line is the calculated profile. Tick marks below the profile mark the positions of allowed reflections. A difference (obs-calc) curve is plotted beneath. Background has been fit as part of the refinement but subtracted prior to plotting.

Results and Discussion

Starting parameters for both refinements were taken from the results of Pei *et al.* (5), though the standard setting of the space

group ($Pnma$) was chosen in the present case. Isotropic thermal parameters were used throughout for all atoms. In addition to the usual parameters, site occupancies were allowed to vary for all atoms (except

TABLE I

REFINED STRUCTURAL PARAMETERS FOR $\text{Yb}_2\text{BaCuO}_5$ AT ROOM TEMPERATURE, SPACE GROUP $Pnma$, $a = 12.0588(1) \text{ \AA}$, $b = 5.6123(1) \text{ \AA}$, $c = 7.0535(1) \text{ \AA}$

Atom	Site	x	y	z	$B(\text{\AA}^2)$
Yb1	4c	0.2883(1)	1/4	0.1180(2)	0.18(2)
Yb2	4c	0.0741(1)	1/4	0.3977(2)	0.25(2)
Ba	4c	0.9056(3)	1/4	0.9292(4)	0.70(6)
Cu	4c	0.6603(2)	1/4	0.7124(3)	0.33(3)
O1	8d	0.4333(2)	-0.0057(4)	0.1648(2)	0.50(3)
O2	8d	0.2268(2)	0.5031(4)	0.3593(3)	0.39(3)
O3	4c	0.1012(2)	1/4	0.0834(4)	0.44(5)

Cu). All sites were found to be fully occupied, within errors, and were therefore fixed at full occupancy during the final refinements cycles. The refinements quickly converged to give excellent fits to the observed profiles (Fig. 1). For $\text{Yb}_2\text{BaCuO}_5$, $R_{\text{wp}} = 4.44\%$, $R_{\text{exp}} = 3.18\%$, for a total of 1862 reflections covering a d -spacing range of 0.52–3.04 \AA . For $\text{Lu}_2\text{BaCuO}_5$, $R_{\text{wp}} = 4.93\%$, $R_{\text{exp}} = 3.65\%$, for 1855 reflections in the same data range. Final refined atomic coordinates for the two phases are given in Tables I and II, with refined interatomic distances presented in Tables III and IV. Both phases are essentially isostructural with Y_2BaCuO_5 (Fig. 2), with small varia-

TABLE II

REFINED STRUCTURAL PARAMETERS FOR $\text{Lu}_2\text{BaCuO}_5$ AT ROOM TEMPERATURE, SPACE GROUP $Pnma$, $a = 12.0314(1) \text{ \AA}$, $b = 5.5989(1) \text{ \AA}$, $c = 7.0380(1) \text{ \AA}$

Atom	Site	x	y	z	$B(\text{\AA}^2)$
Lu1	4c	0.2881(1)	1/4	0.1178(3)	0.41(3)
Lu2	4c	0.0738(2)	1/4	0.3971(3)	0.44(3)
Ba	4c	0.9049(2)	1/4	0.9290(4)	0.82(5)
Cu	4c	0.6597(2)	1/4	0.7123(2)	0.38(3)
O1	8d	0.4330(1)	-0.0050(3)	0.1637(2)	0.52(2)
O2	8d	0.2270(1)	0.5022(4)	0.3597(2)	0.57(3)
O3	4c	0.1010(2)	1/4	0.0833(4)	0.57(4)

TABLE III

METAL–OXYGEN BOND LENGTHS (\AA) IN $\text{Yb}_2\text{BaCuO}_5$

Yb1–O1 $\times 2$	2.286(2)	Ba–O1 $\times 2$	3.220(3)
–O2 $\times 2$	2.337(2)	–O1 $\times 2$	3.022(3)
–O2 $\times 2$	2.299(2)	–O2 $\times 2$	2.934(3)
–O3	2.270(3)	–O2 $\times 2$	2.982(3)
Yb2–O1 $\times 2$	2.267(3)	–O3 $\times 2$	2.8087(2)
–O1 $\times 2$	2.332(2)	–O3	2.597(4)
–O2 $\times 2$	2.342(2)	Cu–O1 $\times 2$	1.976(3)
–O3	2.241(3)	–O2 $\times 2$	2.007(3)
		–O3	2.205(4)

TABLE IV

METAL–OXYGEN BOND LENGTHS (\AA) IN $\text{Lu}_2\text{BaCuO}_5$

Lu1–O1 $\times 2$	2.276(2)	Ba–O1 $\times 2$	3.220(3)
–O2 $\times 2$	2.330(2)	–O1 $\times 2$	3.028(3)
–O2 $\times 2$	2.293(2)	–O2 $\times 2$	2.928(3)
–O3	2.264(3)	–O2 $\times 2$	2.964(3)
Lu2–O1 $\times 2$	2.257(2)	–O3 $\times 2$	2.8017(2)
–O1 $\times 2$	2.326(2)	–O3	2.597(4)
–O2 $\times 2$	2.337(2)	Cu–O1 $\times 2$	1.972(2)
–O3	2.233(3)	–O2 $\times 2$	2.009(2)
		–O3	2.197(3)

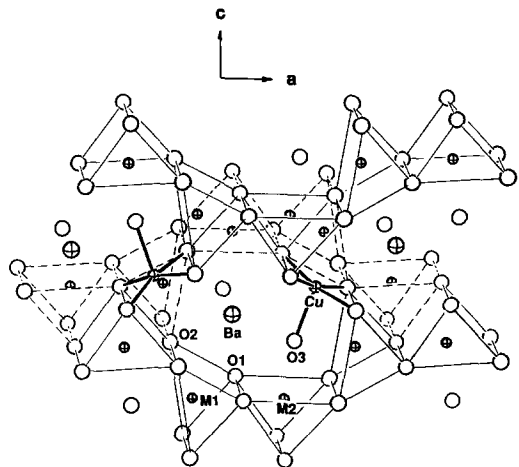


Fig. 2. Structure of $M_2\text{BaCuO}_5$ viewed nearly along the b -axis.

tions in geometry occurring to accommodate the requirements of the smaller rare-earth ions, Yb^{3+} and Lu^{3+} . MO_7 monocapped trigonal prisms share one triangular face to produce M_2O_{11} groups, which are linked by edge-sharing into a three-dimensional network. Cavities within this framework are occupied by Ba, in 11-fold coordination, and Cu in a 5-coordinate, distorted square pyramidal environment. In comparison with the high- T_c phases containing CuO_5 pyramids (8), the distortion of the pyramid is smaller, with basal plane bond lengths in the range 1.972–2.009 Å and apical bond lengths in the range 2.197–2.205 Å, compared to those in $\text{YBa}_2\text{Cu}_3\text{O}_{6.81}$ (9), for example, of 1.928/1.962 Å and 2.303 Å, respectively. There are no direct Cu–O–Cu contacts in the present case. A full description of the structure is given by Michel and Raveau (1).

Acknowledgments

This work is supported by the National Science Foundation, Science and Technology Center for Superconductivity under Grant DMR-88-09854 (PL and SP) and the U.S. Department of Energy, Basic Energy

Sciences–Materials Sciences, under Contract W-31-109-ENG-38(JDJ, YCC, PZJ, and BWV).

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