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The Novel $R_2Ba_{1.25}NiO_{5.25}$ (R = Tm, Yb, Lu) Structure Type

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Crystals of isostructural $R_2Ba_{1.25}NiO_{5.25}$ (R = Tm, Yb, Lu) have been grown and characterized. The crystal structure for R = Yb has been established from X-ray single crystal diffraction data. $R_2Ba_{1.25}NiO_{5.25}$ are tetragonal, S.G. $I4/m$ (No. 87), with unit-cell parameters $a = b$ = 13.582(3), 13.553(4), and 13.549(3) Å, c = 5.656(2), 5.638(2), and 5.633(2) Å, V = 1043.4(8), 1035.6(9), and 1034.1(8) Å^3 for R = Tm, Yb, and Lu, respectively; and Z = 8. Interatomic distances and principal angles are given for the Yb compound. The crystal structure of $Yb_2Ba_{1.25}NiO_{5.25}$ is formed by square NiO_5 pyramids, trigonal YbO_7 prisms capped on one rectangular face, tetragonal bicapped $Ba(1)O_{10}$ prisms, and irregular $Ba(2)O_{10}$ polyhedra. A comparison is made between this structure type and those of Yb_2BaNiO_5 and Y_2BaNiO_5: the RO_7 polyhedra look similar for the three types, and $Yb_2Ba_{1.25}NiO_{5.25}$ contains NiO_5 groups similar to those of Yb_2BaNiO_5 as well as $Ba(2)O_{10}$ units which are shaped like those present at Y_2BaNiO_5.

Introduction

The R_2BaNiO_5 oxides (R = Y, Sm, Gd, Ho, Er, Tm) crystallize in the Nd_2BaNiO_5 structure type (*1–6*) with rather one-dimensional chains of vertex-sharing NiO_6 octahedra which show an unusual twofold distortion: the Ni–O distances to the two axial oxygen atoms are considerably shorter, 0.3 Å, than those to the four equatorial oxygens, and these are distorted from the right angles of a regular octahedron to 79.0(2)° and 77.7(6)° for R = Y, Er, respectively (*5*). These distortions are related to the interesting magnetic properties of these oxides (*5, 7*), and the distances and angles determined for R = Gd have been recently shown (*8*) to be understandable using a model which combines results from molecular-orbital theory, tight-binding band-structure calculations, and empirical atom–atom potential arguments. On the other hand, the R_2BaNiO_5 compounds of Yb and Lu crystallize (*9, 3*) in the Y_2BaCuO_5 structure type, the green phases that frequently appear associated to the 123 superconducting oxides. Hence, in R_2BaNiO_5 (R = Yb, Lu) the Ni atoms show a square pyramidal coordination with Ni–O distances between 1.98 and 2.07 Å (R = Yb) (*9*) or 1.96–2.05 Å (R = Lu) (*3*). Because of their interest in these Ni oxides the authors tried to grow crystals of those formed by the three smallest lanthanides, R = Tm, Yb, Lu, and obtained three

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TABLE I

CRYSTAL DATA FOR TETRAGONAL $R_2Ba_{1.25}NiO_{5.25}$, SPACE GROUP $I4/m$ (No. 87), $Z = 8$

R	Tm	Yb	Lu
M (formula weight)	652.2	660.4	664.3
$a = b$, Å	13.582(3)	13.553(4)	13.549(3)
c, Å	5.656(2)	5.638(2)	5.633(2)
V, Å	1043.4(8)	1035.6(9)	1034.1(8)
$F(000)$	2224	2240	2256
ρ (calcd), g cm^{-3}	8.30	8.47	8.53
μ, cm^{-1}	472.3	486.2	508.0
Cryst dimens, mm	0.030 × 0.030 × 0.040	0.025 × 0.025 × 0.042	0.035 × 0.030 × 0.030

unknown compounds whose crystallographic characterization is the object of this paper. After determining the crystal structure of the Yb compound, they verified that single crystals of the three oxides (R = Tm, Yb, Lu) are isostructural.

Experimental Section

Crystal growth. Black, needle-like, prismatic $R_2Ba_{1.25}NiO_{5.25}$ (R = Tm, Yb, Lu) crystals were grown by reaction of an excess of Ni metal with a mixture of analytical grade R_2O_3 and $BaCO_3$, $R : Ba = 1 : 3$, after heating in air for 3 days at 1200°C and subsequent quenching.

X-Ray structure determinations. Black crystals (R = Tm, Yb, Lu) of prismatic shape were mounted in an Enraf–Nonius CAD 4 diffractometer and were studied using graphite-monochromated Mo$K\alpha$ radiation ($\lambda = 0.71069$ Å) at 21°C. The cell dimensions were refined by least-squares fitting the 2θ values of 25 reflections. A summary of the fundamental crystal data is given in Table I. For R = Tm, Yb and Lu, an I-cell was determined from the systematic extinctions, and the measurement of the intensities of the equivalent reflections showed tetragonal symmetry. Table II shows the refinement data for the Yb compound, whose intensities were corrected for Lorentz and polarization effects. Scattering factors for neutral atoms and anomalous dispersion corrections for Yb, Ba, and Ni were taken from the "International Tables for X-Ray Crystallography" (*10*). The structure was solved by Patterson and Fourier methods. The centrosymmetric space group $I4/m$ (No. 87) was obtained during the course of the structure solution. An empirical absorption correction (*11*) was applied at the end of the isotropic refinement. The maximum and minimum absorption factors were 1.890 and 0.718, respectively. Final mixed full-matrix least-squares refinement with anisotropic temperature factors for all atoms except O1 and O2, and weights (*12*) $w = w_1w_2$, where $w_1 = 1/(a + b|F_0|)^2$ and $w_2 = 1/(c + d(\sin\theta/\lambda))$, and the coefficients shown in Table III. A final difference synthesis shows a maximum electron density of 3e Å^{-3} located at the Ba(1) position. Most

TABLE II

REFINEMENT DATA FOR $Yb_2Ba_{1.25}NiO_{5.25}$

Scan technique	$\Omega/2\theta$
Data collected	(0,0,0) to (19,19,7)
Unique data	804
Unique data, $(I) > 2\sigma(I)$	656
Standard reflections	3/57 reflections
R_f, %	4.3
R_{wf}, %	4.9
Average shift/error	0.003

TABLE III

COEFFICIENTS FOR THE WEIGHTING SCHEME IN $Yb_2Ba_{1.25}NiO_{5.25}$

	a	*b*		*c*	*d*
$\lvert F_o \rvert < 123$	21.65	−0.13	$(\sin \theta)/\lambda < 0.40$ Å^{-1}	4.16	−7.46
$123 < \lvert F_o \rvert < 1437$	2.72	0.03	$0.40 < (\sin \theta)/\lambda < 0.71$	0.25	0.88

of the calculations were carried out with the X-ray 80 system (*13*).

Results and Discussion

Table IV includes the atomic parameters obtained for $Yb_2Ba_{1.25}NiO_{5.25}$. Interatomic distances and principal angles are shown in Table V. The coordination polyhedra for the metals are: square NiO_5 pyramids with Ni atoms at 0.370(3) Å from the base and Ni–O distances between 1.978 Å and 2.045 Å; $Yb(1)O_7$ and $Yb(2)O_7$ trigonal prisms monocapped on one rectangular face [$Yb(2)O_7$, slightly smaller than $Yb(1)O_7$, is shown in Fig. 1]; and tetragonal bicapped $Ba(2)O_{10}$ prisms as well as irregular $Ba(1)O_{10}$ polyhedra (Fig. 2). The crystal structure of $Yb_2Ba_{1.25}NiO_{5.25}$ can be conceived as formed by columns along the *c* direction. In these, $Ba(2)O_{10}$ polyhedra alternate with units that are constituted by four $Yb(2)O_7$ polyhedra which have in common the apical vertex, O(1), and thus share triangular faces. This oxygen atom, O(1), is also an apical vertex of the $Ba(2)O_{10}$ polyhedron. Every four of these units, those with equal *z* value, occupy the vertices of a large square, that is, the (001) face of the unit-cell, and connect each other in the *xy* plane according to the sequence Yb(2)–Yb(1)–Ni–Yb(1)–Yb(2); the $Yb(2)O_7$ polyhedra share edges, and $Yb(1)O_7$ and NiO_5 alternatively have common faces or edges, in such a way that a fifth column raises in the center of the square

TABLE IV

ATOMIC PARAMETERS FOR $Yb_2Ba_{1.25}NiO_{5.25}$

$U_{eq} = (1/3)\Sigma[U_{ij}a_i^*a_j^*a_ia_j\cos(a_i, a_j)] \times 10^3$

Atom	Site	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq}
Yb1	8h	0.2499(1)	0.1668(1)	0.0000(0)	8.0(3)
Yb2	8h	0.4119(1)	0.3569(1)	0.0000(0)	8.1(3)
Ba1	8h	0.1387(1)	0.4618(1)	0.0000(0)	9.7(4)
Ba2	2a	0.0000(0)	0.0000(0)	0.0000(0)	9.7(7)
Ni	8h	0.0412(2)	0.2448(2)	0.0000(0)	8(1)
O1	2b	0.5000(0)	0.5000(0)	0.0000(0)	7(5)
O2	8h	0.3677(10)	0.0377(11)	0.0000(0)	9(2)
O3	16i	0.1472(7)	0.2591(7)	0.2456(18)	10(2)
O4	16i	0.1788(7)	0.0470(7)	0.2476(21)	11(2)

TABLE V

INTERATOMIC DISTANCES *d* (Å), THE NUMBER OF EQUAL METAL–OXYGEN DISTANCES (*n*), AND PRINCIPAL ANGLES (DEG) FOR $Yb_2Ba_{1.25}NiO_{5.25}$

	d	*n*		*d*	*n*
Yb1 –O2	2.368	×1	Ba1–O4	2.856	×2
–O3	2.329	×2	–O2	2.711	×1
–O4	2.348	×2	–O3	3.207	×2
–O3	2.239	×2	–O2	2.686	×1
Yb2 –O1	2.277	×1	Ba2–O4	2.868	×8
–O3	2.274	×2	–O1	2.819	×2
–O4	2.286	×2	Ni –O3	2.004	×2
–O4	2.369	×2	–O2	1.978	×1
Ba1 –O3	3.080	×2	–O4	2.045	×2
–O2	2.820	×2			

Angles

O3–Ni–O3	87.4
O3– –O2	107.8
O3– –O4	89.4
O3– –O4	158.9
O2– –O4	93.0
O4– –O4	86.1

Note. Standard deviations are 0.011 Å and 0.40° for lengths and angles, respectively.

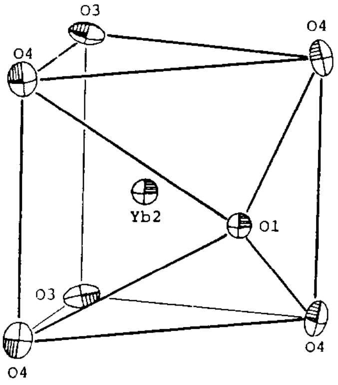

FIG. 1. $Yb(2)O_7$ coordination polyhedron in $Yb_2Ba_{1.25}NiO_{5.25}$.

with the same alternance as the other four but displaced a distance of $z = \frac{1}{2}$. Every two adjacent cells house pairs of $Ba(1)O_{10}$ polyhedra which share the (O2)–O(2) edge (upper part of Figure 2) and remain mutually twisted 90° along the c-axis. A schematic representation of the connections between the coordination polyhedra of the metals along the c-axis is shown in Fig. 3.

The crystal structure of $Yb_2Ba_{1.25}NiO_{5.25}$ (I) can be compared with those established (*9, 5*) for Yb_2BaNiO_5 (II) and Y_2BaNiO_5 (III) looking at the coordination polyhedra present in each one. The RO_7 (R = Yb, Y) polyhedra are very similar in the three cases, and show R–O average distances of 2.310 Å for I and II (R = Yb), and 2.531 Å for III (R = Y). I and II include two kinds of YbO_7 polyhedra, one of them slightly smaller than the other. On the contrary, all the YbO_7 polyhedra are equally sized in III. The Ni coordinations are either square pyramidal (I, II) or flattened octahedral (III) with mean Ni–O distances (Å) of 2.015, 2.022, and 2.082, for I, II, and III, respectively. The NiO_5 quadrangular pyramids (I, II) show similar Ni–O distances and are isolated units, which join themselves through YbO_7 and BaO_{10} polyhedra as above indicated and can be seen in Fig. 3. On the contrary, the NiO_6 octahedra (III) form chains by sharing apical vertices, these lying from the Ni atom at a distance 0.3 Å smaller than the equatorial oxygens. As II and III include only one kind of Ba polyhedron, BaO_{11} in II and BaO_{10} in III, with average Ba–O distances (Å) of 2.940 and 2.923, respectively, there are two different Ba atoms in I, eight Ba(1) and two Ba(2) per unit-cell. Both coordinate to 10 oxygens at average

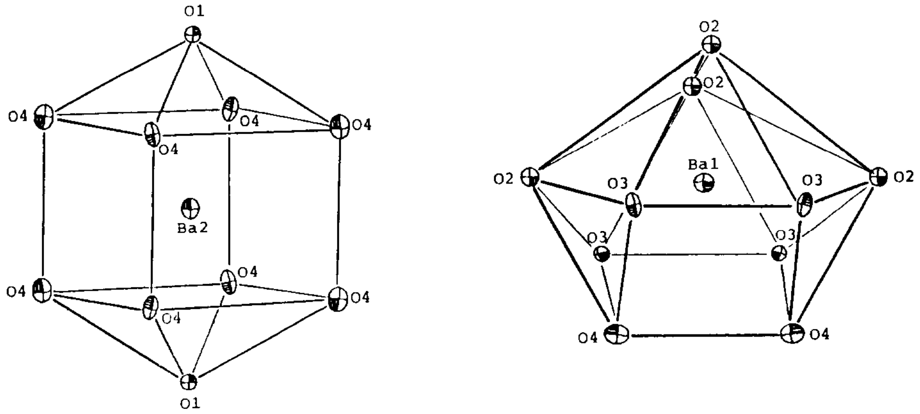

FIG. 2. BaO_{10} coordination polyhedra (14) for Ba(1) (right) and Ba(2) (left) in $Yb_2Ba_{1.25}NiO_{5.25}$.

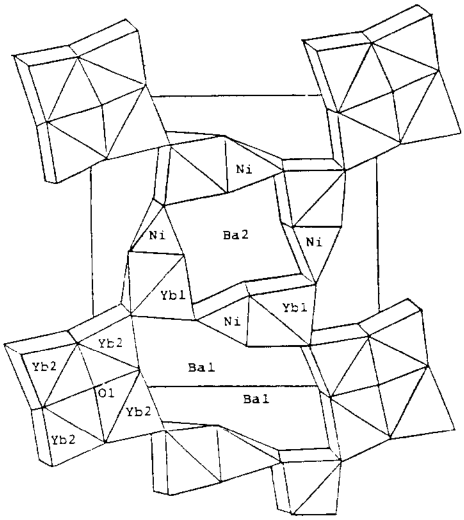

FIG. 3. Schematic representation of the connections along the c-axis between the coordination polyhedra of the metals in $Yb_2Ba_{1.25}NiO_{5.25}$.

distances (Å) of 2.932 and 2.858, respectively. In conclusion, the novel structure type can be considered as an intermediate between the Yb_2BaNiO_5 and Y_2Ba NiO_5 types.

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