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Er_2BaNiO_5: Structure Refinement Using Neutron Powder Diffraction Data

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Abstract. The crystal structure of dierbium barium nickelate, Er_2BaNiO_5, has been refined from neutron powder diffraction data, collected at room temperature. Results agree with those obtained from single-crystal X-ray diffraction. Sixfold oxygen coordination around the Ni atoms is confirmed and more precise oxygen positions are given. The NiO_6 octahedra show an unusual twofold distortion: the Ni—O distances to the two axial O atoms are considerably shorter, by 0·3 Å, than those to the four equatorial oxygens; these oxygens are distorted from the right angles of a regular octahedron to 79·1 (1)°. Interesting physical properties are suggested by the existence of infinite isolated chains of NiO_6 flattened octahedra sharing vertices in the direction of the *a* axis, with extremely short, 3·75 Å, Ni—O(axial)—Ni distances. Orthorhombic, *Immm*, $a = 3{\cdot}7541$ (1), $b = 5{\cdot}7442$ (1), $c = 11{\cdot}3019$ (2) Å, $V = 243{\cdot}71$ (2) Å^3, $Z = 2$, $\lambda = 1{\cdot}594$ Å, $R_{wp} = 7{\cdot}52\%$.

Introduction. The Nd_2BaNiO_5 structure type (orthorhombic, *Immm*) was first described by Schiffler & Müller-Buschbaum (1986*a*). Subsequent studies by these authors (Schiffler & Müller-Buschbaum, 1986*a*,*b*, 1987; Müller-Buschbaum & Lang, 1988; Müller-Buschbaum & Rüter, 1989), established this structure for the compounds formed with rare earth from Sm to Tm. Independently, Amador (1989) prepared and characterized polycrystalline samples of nine R_2BaNiO_5 oxides, with R = Y, Nd, Sm, Eu, Gd, Dy, Ho, Er or Tm; a better refinement of the Gd_2BaNiO_5 crystal structure was performed (Amador *et al.*, 1989) and the structure of the yttrium compound was established by single-crystal X-ray diffraction (Amador *et al.*, 1990).

In these compounds, Ni atoms are placed at the centers of flattened oxygen octahedra showing two extremely short Ni—O distances (*i.e.* 1·89 Å for the Gd compound). These polyhedra, rather peculiar in nickel crystallochemistry, particularly contrast with the fivefold oxygen environment of Cu in the isostoichiometric compounds R_2BaCuO_5 (R = Y or rare-earth elements) (Campá *et al.*, 1988), the so-called 'green phases'. The distortions present in the NiO_6 octahedra of the Gd compound (Amador *et al.*, 1989) have recently been shown (Burdett & Mitchell, 1990) to be understandable in terms of a model which combines the results of molecular orbital theory, tight-binding band-structure calculations, and empirical atom–atom potential arguments. In order to check the oxygen stoichiometry and the coordination, especially around Ni atoms, and to confirm both the symmetry and the space group, a neutron powder diffraction study of the erbium compound has been undertaken. The crystal structure of this compound is known (Schiffler & Müller-Buschbaum, 1987), but was determined with a high R factor, 0·103.

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Experimental. The sample was prepared from a stoichiometric mixture of analytical grade Er_2O_3, BaO_2 and NiO, which was ground, shaped into pellets and heated in air at 1173, 1273, 1373 and 1473 K. After each thermal treatment (12 h), the products were quenched, reground and shaped into pellets.

The neutron powder diffraction data of Er_2BaNiO_5 were collected with the *D2B* diffractometer (Hewat, 1986) at ILL/Grenoble, working in high-intensity mode, at 295 K. A wavelength of 1·594 Å (germanium monochromator, [533] planes) was selected. The angular range was $10 \leq 2\theta \leq 146°$, with steps of 0·05° in 2θ.

The Rietveld method (Rietveld, 1969) and the Young & Wiles (1982) program were employed in the profile refinement. A pseudo-Voigt function was chosen to generate the line shape of the diffraction peaks. The coherent scattering lengths of Er, Ba, Ni and O are, respectively, 8·030, 5·250, 10·300 and 5·805 fm.

The background was estimated by linear interpolation between points corresponding to regions devoid of reflections. Since the presence of small amounts of Er_2O_3 (cubic, $a = 10·5457$ Å, $Ia\bar{3}$) and NiO (cubic, $a = 4·1792$ Å, $Fm\bar{3}m$) was detected in the pattern, the profile refinement of the mixture was performed.

Table 1. *Structural parameters for* Er_2BaNiO_5 *at* 295 K

	Site	x	y	z	Occupation	B(Å^2)
Ba	2(d)	0	$\frac{1}{2}$	0	1	0·62 (7)
Er	4(i)	0	0	0·2028 (2)	1	0·21 (3)
Ni	2(b)	$\frac{1}{2}$	0	0	1	0·29 (4)
O1	8(l)	$\frac{1}{2}$	0·2418 (5)	0·1487 (2)	1·006 (3)	0·31 (3)
O2	2(a)	0	0	0	0·99 (1)	0·45 (4)

$a = 3·7541$ (1), $b = 5·7442$ (1), $c = 11·3019$ (2) Å.

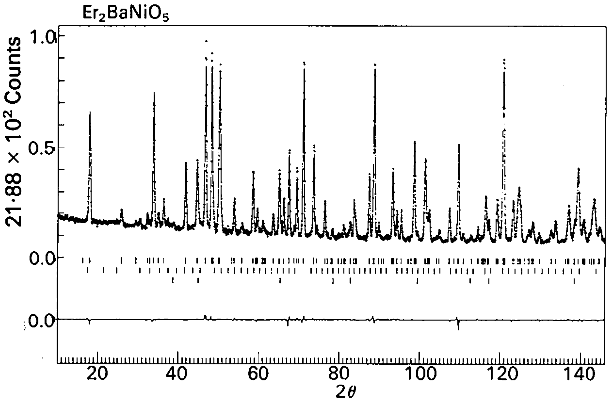

Fig. 1. Observed (crosses), calculated (solid line) and difference (at the bottom) neutron diffraction profiles for Er_2BaNiO_5 at 295 K. The three series of thin marks indicate the positions of the allowed Bragg reflections for Er_2BaNiO_5, Er_2O_3 and NiO, from top to bottom.

A total of 22 parameters were refined, including zero-point, half-width and pseudo-Voigt parameters for the peak shape; scale factor, positional parameters, isotropic thermal parameters, oxygen occupancy factors and unit-cell parameters for Er_2BaNiO_5, and scale factors and unit-cell parameters for Er_2O_3 and NiO were refined.

In the final refinement cycle, the shifts in the atomic parameters were zero up to the fourth decimal place.

Discussion. The neutron diffraction pattern of Er_2BaNiO_5 was analyzed in the space group *Immm*. The final atomic coordinates and isotropic thermal factors are listed in Table 1.*

The observed and calculated profiles of the pattern are shown in Fig. 1. Final profile R factors, R_p and R_{wp} (Young & Wiles, 1982) were 5·88 and 7·52%

Table 2. *Selected distances* (Å) *and angles* (°) *in* Er_2BaNiO_5 *at* 295 K

Ba polyhedron		Ni polyhedron	
8 × Ba—O1	2·924 (2)	4 × Ni—O1	2.180 (3)
2 × Ba—O2	2·8715 (1)	2 × Ni—O2	1.8770 (1)
Er polyhedron			
		2 × O1—Ni—O1	180·0
4 × Er—O1	2·414 (2)	2 × O1—Ni—O1	100·8 (2)
2 × Er—O1	2·240 (3)	2 × O1—Ni—O1	79·1 (1)
1 × Er—O2	2·292 (2)	8 × O1—Ni—O2	90·0
		O2—Ni—O2	180·0

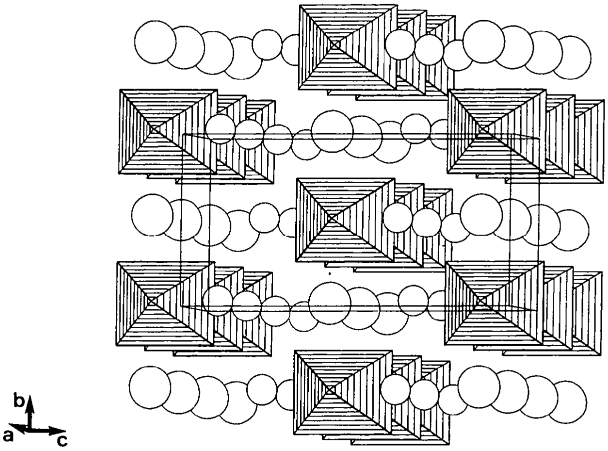

Fig. 2. View of the structure of Er_2BaNiO_5, showing the one-dimensional chains of vertex-sharing NiO_6 octahedra in the direction of the a axis. Small circles represent Er atoms, and large circles Ba atoms.

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* The integrated intensity of each Bragg reflection on the profile and powder data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53449 (7 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

(expected, 4·10%), R factors for the integrated intensity and structure factors, R_I and R_F, were 7·36 and 5·34%, respectively, for 151 reflections. From the scale factors of the impurities, volume ratios Er_2O_3:Er_2BaNiO_5 = 0·032:1 and NiO:Er_2BaNiO_5 = 0·015:1 were calculated.

The results obtained from the neutron powder refinement are consistent with those previously determined by single-crystal X-ray diffraction (Schiffler & Müller-Buschbaum, 1987). Standard deviations of the oxygen positions are about six times smaller in the present study. No extra lines have been observed in the powder pattern, which confirms the symmetry and space group. Small irregularities in the background are thought to be due to the presence of small amounts of a glassy phase, probably related to BaO, remaining from the incomplete reaction between the starting reagents.

Bonding distances and angles for the polyhedra around the metallic atoms are given in Table 2. The most surprising feature in this structural type is the abnormal coordination of nickel, which is in a flattened octahedron of O atoms, $Ni(O1)_4(O2)_2$. In the erbium compound, nickel is coordinated to four O atoms at 2·180 Å and two more at shorter distances, 1·877 Å. Nickel octahedra form independent chains along the a axis *via* O2, as shown in Fig. 2. O1 and O2 positions are fully occupied within one and two standard deviations, respectively, which confirms the oxygen stoichiometry and sixfold coordination of nickel.

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Structure of $MgCl_2.RbCl.6H_2O$

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Abstract. Magnesium rubidium trichloride hexahydrate, M_r = 324·22, triclinic, $P1$, a = 6·672 (5), b = 13·282 (15), c = 6·639 (5) Å, α = 89·83 (8), β = 91·72 (6), γ = 90·41 (8)°, V = 588·0 (14) Å^3, Z = 2, D_x = 1·831 Mg m^{-3}, $\bar{\lambda}$(Mo $K\alpha$) = 0·71073 Å, μ = 5·17 mm^{-1}, $F(000)$ = 320, T = 253 K, $R(F)$ = 0·078 for 2604 independent reflections with $|F_o| > 3\sigma(|F_o|)$. The crystal consists of a network of top-sharing [$RbCl_6$] octahedra and isolated $[Mg(H_2O)_6]^{2+}$ octahedra occupying holes in the

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