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$Eu_{1.8}La_{0.2}BaZnO_5$: a Rietveld refinement using X-ray powder diffraction

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The families of oxides with stoichiometry RE_2BaMO_5 (where RE is a trivalent rare earth, and M is Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pd^{2+} or Pt^{2+}) are known as the green phases in studies of Y–Ba–Cu–O superconductor ceramics. These oxides are not superconductors but nevertheless present interesting structural types. In this work, the synthesis and structural characterization using the Rietveld method applied to X-ray powder diffraction data for $Eu_{1.8}La_{0.2}BaZnO_5$ (europium lanthanum barium zinc oxide) are presented. The compound is isostructural with Y_2BaZnO_5. The two sites for Y^{3+} are occupied by Eu^{3+}, while La^{3+} ions partially occupy one of these sites.

Key indicators

Powder X-ray study
T = 300 K
Mean σ(Zn—O) = 0.014 Å
R factor = 0.091
wR factor = 0.12
Data-to-parameter ratio = 23.3

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Eu_2BaZnO_5 belongs to the family of mixed oxides with general stoichiometry RE_2BaMO_5, in which four different structural types are possible depending on the RE^{3+} and/or M^{2+} ions present in the crystal structure. Each of them is characterized by different coordination polyhedra around the M^{2+} cation (Burdett & Mitchell, 1990; Saez-Puche & Hernandez-Velazco, 1994; Lavat *et al.*, 1992). For type I (Sm_2BaCuO_5 type), the M^{2+} ions form isolated MO_5 square-pyramidal units in an orthorhombic unit cell, space group *Pnma*, and $Z = 4$. For type II (Nd_2BaNiO_5 type), the M^{2+} ions form infinite chains of MO_6 octahedra, running parallel to the *a* axis and also with an orthorhombic unit cell, with space group *Immm* and $Z = 2$. In the case of type III (Nd_2BaPtO_5 type), the symmetry is tetragonal, space group *P4/mbm*, $Z = 2$, in which M^{2+} ions are in isolated MO_4 square-planar environments. For the last type, type IV (Nd_2BaZnO_5 type), the symmetry is also tetragonal, with space group *I4/mcm* and $Z = 4$. In that structure, the M^{2+} ions are in isolated MO_4 tetra-

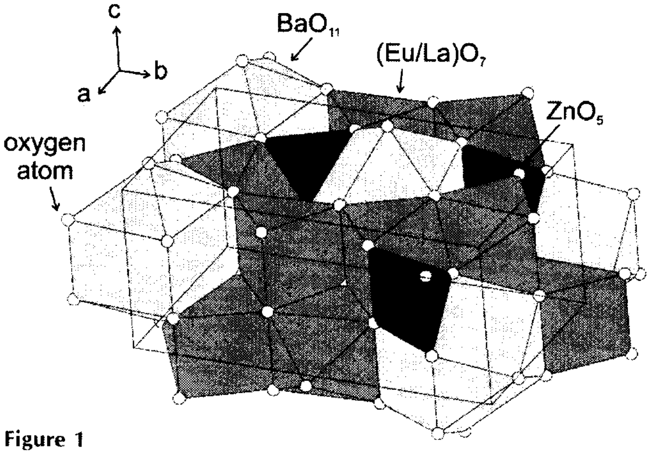

Figure 1
The unit-cell contents of $Eu_{1.8}La_{0.2}BaZnO_5$.

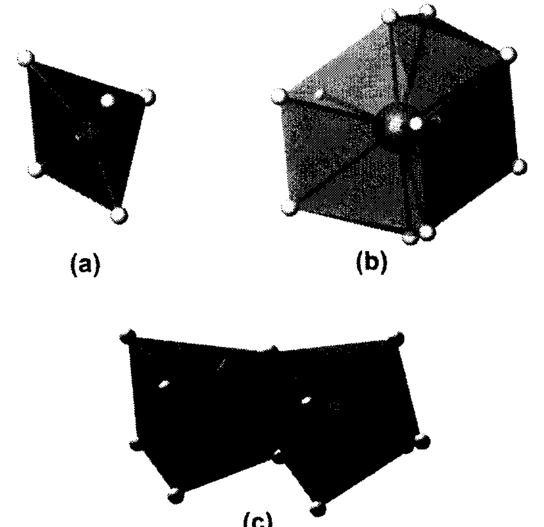

Figure 2
The coordination polyhedra present in $Eu_{1.8}La_{0.2}BaZnO_5$. (*a*) ZnO_5, distorted square-based pyramid. (*b*) BaO_{11}, a type of distorted tricapped quadrangular prism. (*c*) EuO_7 and Eu/LaO_7 non-equivalent distorted monocapped quadrangular prisms.

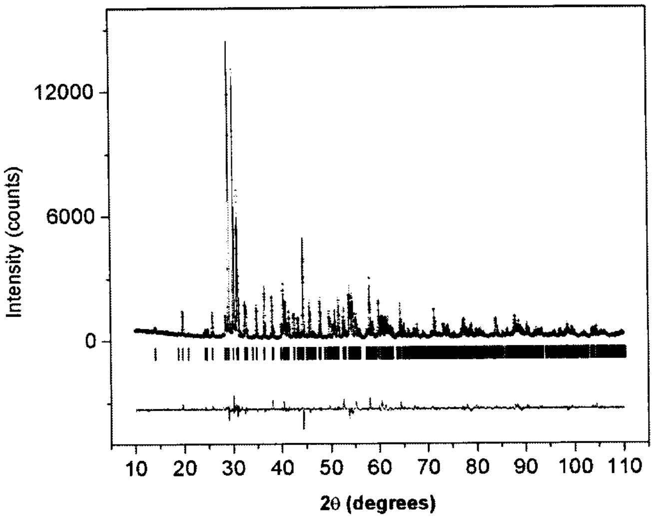

Figure 3
A comparison of observed (cross symbols) and calculated (solid line) intensities for $Eu_{1.8}La_{0.2}BaZnO_5$. The difference pattern appears below. The Bragg peak positions for $Eu_{1.8}La_{0.2}BaZnO_5$ and PtO_2 are represented as vertical marks.

hedra. Due to their structural features and interesting properties, this family of compounds has previously been studied and characterized. However, no report exists to date on the crystallographic characterization of the solid solution of Eu_2BaZnO_5 with La^{3+}, which we report here for the case of $Eu_{1.8}La_{0.2}BaZnO_5$.

The replacement mechanism seems to be given by $Eu^{3+} \longleftrightarrow La^{3+}$. According to this mechanism, the solid solution has the formula $Eu_{2-x}La_xBaZnO_5$ with $0 < x < 0.3$. The solubility range is small, taking into account our preliminary X-ray diffraction analysis: the cell parameters for $x = 0$, 0.2 and 0.3 decrease with x content, following Vegard's law.

The crystal structure of $Eu_{1.8}La_{0.2}BaZnO_5$ is shown in Fig. 1, which also shows a view of the unit-cell contents. The introduction of the La^{3+} ions generates changes in the unit-cell parameters compared with the data reported by Kaduk *et al.* (1999) for Eu_2BaZnO_5: $a = 7.1789$ (1) Å, $b = 12.53575$ (17) Å, $c = 5.79103$ (8) Å and $V = 521.15$ Å^3 (Kaduk *et al.*, 1999); parameters from the present work for $Eu_{1.8}La_{0.2}BaZnO_5$: $a = 7.1952$ (1) Å, $b = 12.5720$ (2) Å, $c = 5.8035$ (1) Å and $V = 524.97$ (1) Å^3.

The structure of $Eu_{1.8}La_{0.2}BaZnO_5$ exhibits three different coordination polyhedra, namely a distorted square-based pyramidal ZnO_5 (Fig. 2*a*), a type of distorted tricapped quadrangular prismatic BaO_{11}, in which Ba ions are surrounded by 11 O atoms (Fig. 2*b*), and two non-equivalent distorted monocapped trigonal prisms (Fig. 2*c*), one of them completely occupied by Eu^{3+} (the EuO_7 polyhedron) and the other with partial substitution of La^{3+} ions (the Eu/LaO_7 polyhedron). This last fact can be supported by the following observations. The average bond distance for EuO_7 polyhedra is 2.35 Å, very close to the sum of the ionic radii reported by Shannon (1976) ($r_{Eu} + r_O = 1.01 + 1.38 = 2.39$ Å). In the second monocapped trigonal prism, Eu/LaO_7, the average bond is longer (2.38 Å). This distortion is due to the incorporation of the La^{3+} ions on this site. In the same way, the average bond distances found in BaO_{11} and ZnO_5 polyhedra fit reasonably well with the sum of their ionic radii: mean Ba—O = 3.08 Å, compared with $r_{Ba} + r_O = 2.95$ Å, and mean Zn—O = 2.07 Å, compared with $r_{Zn} + r_O = 2.06$ Å. These average bond distances are similar to those reported for Eu_2BaZnO_5 by Kaduk *et al.* (1999).

Experimental

The title compound was synthesized by a solid-state reaction. Stoichiometric quantities of 0.6093, 0.4595, 2.7834 and 1.1478 g for the starting reactants Eu_2O_3 (99.99%, Aldrich), La_2O_3 (99.99%, Aldrich), $BaCO_3$ (99.99%, Aldrich) and ZnO (99.99%, Aldrich), respectively, with a total weight of 5 g, were mixed with acetone for at least 10 min and then powdered in an agate mortar. The powder was heated for a few hours in air at 973 K using a platinum crucible in order to expel CO_2. Finally, the compound was fired at 1473 K for 2–3 d. Because $Eu_{1.8}La_{0.2}BaZnO_5$ can be easily hydrated, it was kept in a desiccator.

Crystal data

$Eu_{1.8}La_{0.2}BaZnO_5$
$M_r = 584.03$
Orthorhombic, *Pbnm*
$a = 7.1952$ (1) Å
$b = 12.5720$ (2) Å
$c = 5.8035$ (1) Å
$V = 524.97$ (1) Å^3
$Z = 4$
$D_x = 7.4$ (1) Mg m^{-3}

Cu $K\alpha$ radiation
$\mu = 226.2$ mm^{-1}
$T = 300$ K
Specimen shape: flat sheet
20 × 20 × 0.2 mm
Specimen prepared at 1473 K
Particle morphology: homogeneous micrometric particles, pale yellow

Data collection

Siemens D5000 diffractometer
Specimen mounting: packed powder sample container
Specimen mounted in reflection mode

$h = 0 \rightarrow 9$
$k = 0 \rightarrow 16$
$l = 0 \rightarrow 7$
$2\theta_{min} = 10$, $2\theta_{max} = 110°$
Increment in $2\theta = 0.02°$

Refinement

Refinement on $I_{\rm net}$
$R_{\rm p} = 0.091$
$R_{\rm wp} = 0.12$
$R_B = 0.071$
$S = 1.67$
$2\theta_{\rm min} = 10.0248$, $2\theta_{\rm max} = 110.0248°$
Increment in $2\theta = 0.02°$
Profile function: pseudo-Voigt, modified by Thompson *et al.* (1987)
791 reflections
34 parameters
Weighting scheme based on measured s.u. values
Preferred orientation correction: none

Table 1
Selected bond lengths (Å).

Eu1—O1	2.28 (2)	Ba—O1$^{\rm ix}$	3.38 (1)
Eu1—O1$^{\rm i}$	2.28 (2)	Ba—O1$^{\rm x}$	3.38 (1)
Eu1—O2	2.37 (1)	Ba—O1$^{\rm xi}$	3.24 (1)
Eu1—O2$^{\rm ii}$	2.39 (1)	Ba—O2$^{\rm ix}$	2.96 (1)
Eu1—O2$^{\rm iii}$	2.39 (1)	Ba—O2$^{\rm xii}$	3.07 (1)
Eu1—O2$^{\rm i}$	2.37 (1)	Ba—O2$^{\rm xiii}$	3.07 (1)
Eu1—O3	2.40 (2)	Ba—O2$^{\rm x}$	2.96 (1)
La—O1$^{\rm iv}$	2.31 (1)	Ba—O3$^{\rm xiv}$	2.78 (2)
La—O1$^{\rm v}$	2.47 (2)	Ba—O3$^{\rm xii}$	2.904 (1)
La—O1$^{\rm vi}$	2.47 (2)	Ba—O3$^{\rm xv}$	2.904 (1)
La—O1$^{\rm vii}$	2.31 (1)	Zn—O1$^{\rm xv}$	2.00 (1)
La—O2	2.43 (1)	Zn—O1$^{\rm xvi}$	2.00 (1)
La—O2$^{\rm i}$	2.43 (1)	Zn—O2$^{\rm xii}$	2.15 (1)
La—O3	2.25 (2)	Zn—O2$^{\rm xiii}$	2.15 (1)
Ba—O1$^{\rm viii}$	3.24 (1)	Zn—O3$^{\rm xvii}$	2.05 (2)

Symmetry codes: (i) $x, y, \frac{1}{2} - z$; (ii) $x - \frac{1}{2}, \frac{1}{2} - y, 1 - z$; (iii) $x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$; (iv) $\frac{1}{2} + x, \frac{1}{2} - y, -z$; (v) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$; (vi) $\frac{1}{2} - x, y - \frac{1}{2}, z$; (vii) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$; (viii) $\frac{1}{2} + x, \frac{3}{2} - y, -z$; (ix) $\frac{3}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (x) $\frac{3}{2} - x, \frac{1}{2} + y, z$; (xi) $\frac{1}{2} + x, \frac{3}{2} - y, \frac{1}{2} + z$; (xii) $1 - x, 1 - y, z - \frac{1}{2}$; (xiii) $1 - x, 1 - y, 1 - z$; (xiv) $1 + x, 1 + y, z$; (xv) $1 - x, 1 - y, \frac{1}{2} + z$; (xvi) $1 - x, 1 - y, -z$; (xvii) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$.

The starting set of parameters to perform a Rietveld refinenment for $Eu_{1.8}La_{0.2}BaZnO_5$ was taken from the data reported by Kaduk *et al.* (1999) for the isostructural compound Eu_2BaZnO_5. The structure was refined against the powder diffraction data by the Rietveld method, using a pseudo-Voigt function modified by Thompson *et al.* (1987) to generate the line shape of the diffraction peaks. The background was initially refined by means of a linear interpolation between 70 background points with refinable heights. At the end of the refinement, the values for all of these background heights were fixed. The refinement was performed by describing the symmetry in the space group *Pbnm* (No. 62), which is a non-standard setting (*cab* axis reordering) for the standard symbol *Pnma*. We used this setting in order to facilitate a comparison with other previously reported isostructural compounds, in which the *Pbnm* setting was also used, *e.g.* Y_2BaZnO_5 (Michel & Raveau, 1983), Dy_2BaZnO_5 (Mueller-Buschbaum & Rabbow, 1993), Ho_2BaZnO_5 and Er_2BaZnO_5 (Wong-Ng *et al.*, 1998), and Eu_2BaZnO_5, Sm_2BaZnO_5, Gd_2BaZnO_5 and Tm_2BaZnO_5 (Kaduk *et al.*, 1999). The following parameters were refined: zero point, scale factor, unit-cell dimensions, half-width, pseudo-Voigt parameters for the peak shape, and positional and isotropic displacement parameters. For the occupation factors, we started the refinement considering the amount of La^{3+}, equally distributed over the two Eu^{3+} sites in Eu_2BaZnO_5 (*i.e.* 0.9 and 0.1 for Eu^{3+} and La^{3+}, respectively, in each of the two sites). Keeping the occupation factors fixed, we found unreasonable isotropic displacement parameters, *i.e.* very high on one site and very low (almost negative) on the other. Because atomic sites corresponding to smaller or negative values of displacement parameters can be interpreted as sites in which elements of higher atomic numbers should be located, we tried to improve our results by placing all the La^{3+} cations in the site with the higher displacement parameter (with occupation factors of 0.8 for Eu^{3+} and 0.2 for La^{3+}), keeping the other site with Eu^{3+} cations only (occupation factor of 1.0). In this way, we found reasonable displacement parameters. Refinement of the occupation factors was not included in the final refinement because it did not allow the attainment of stable behaviour, so convergence was not reached. The fixed occupation factors for the Eu^{3+} and La^{3+} cations cited above were assigned according to the data estimated from the composition of the reactants used. These findings are in agreement with the longer bonds found on the site with incorporated La^{3+} cations, as mentioned in the *Comment* section. A small quantity of PtO_2 was refined as a secondary phase, a product of a chemical reaction with the crucible employed. The data for the refinement of this secondary phase were obtained from the data reported for β-PtO_2 by Siegel *et al.* (1969). According to the refinement, the weight fractions for $Eu_{1.8}La_{0.2}BaZnO_5$ and PtO_2 were 99.5 (1) and 0.5 (1)%, respectively. The results of the Rietveld refinement are shown in Fig. 3.

Data collection: *DIFFRAC/AT* (Siemens, 1993); cell refinement: *DICVOL91* (Boultif & Louer, 1991); program(s) used to refine structure: *FULLPROF* (Rodríguez-Carvajal, 1990); molecular graphics: *ATOMS* (Dowty, 2000); software used to prepare material for publication: *ATOMS*.

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