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$(\text{Ca}_{1-x}\text{Pr}_x)_2(\text{Co}_{1-y}\text{Al}_y)_2\text{O}_5$, a Brownmillerite Structure

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Abstract. Aluminium calcium cobalt praseodymium oxide, $(\text{Ca}_{0.821(4)}\text{Pr}_{0.179})_2\{\text{Co}[\text{Co}_{0.651(16)}\text{Al}_{0.349}]\}_2\text{O}_5$, $M_r = 303.0$, orthorhombic, $Pnma$, $a = 5.2789$ (5), $b = 14.998$ (2), $c = 5.4868$ (5) Å, $V = 434.41$ (14) Å³, $Z = 4$, $D_x = 4.63$ g cm⁻³, $\lambda(\text{Mo K}\alpha) = 0.71069$ Å, $\mu = 102.5$ cm⁻¹, $F(000) = 572.4$, room temperature, $R = 0.0484$, $wR = 0.0461$ for 398 reflections $> 4\sigma(F_o)$. The Co^{3+} occupies the octahedral site, while Co^{2+} and Al^{3+} occupy the tetrahedral site. The octahedron is elongated nearly parallel to the b axis, Co1—O2 2.190 (6) Å and the equatorial bond lengths to O1 are 1.870 (10) and 1.957 (10) Å respectively. The tetrahedron around Co/Al is severely distorted. The octahedral layers are linked by the tetrahedra as found in brownmillerite. The eight oxygen ions coordinated to $\text{Ca}^{2+}/\text{Pr}^{4+}$ form an irregular polyhedron, with Ca/Pr—O bond lengths varying from 2.337 (9) to 2.818 (10) Å. To stabilize the brownmillerite structure in the Ca—Co—O system both Pr and Al are necessary. Single phase material for $(\text{Ca}_{1-x}\text{Pr}_x)_2(\text{Co}_{1-y}\text{Al}_y)_2\text{O}_5$ can be synthesized at 1400 K for $0.15 < x < 0.2$ and $0.15 < y < 0.25$. The phase decomposes at 1473 K.

Experimental. While attempting the synthesis of $\text{YBa}_2\text{Cu}_3\text{O}_7$ -like phases in the oxide system Pr—Ca—Cu—Co, platy, black single crystals were observed in the reaction product when a mixture of $\frac{1}{6}\text{Pr}_6\text{O}_{11} : 2\text{CaCO}_3 : 2\text{CuO} : \frac{1}{3}\text{Co}_3\text{O}_4$ with 10 wt % PbO as flux was heated at 1333 K for 12 h in an alumina boat and then furnace cooled to room temperature. The crystals formed in the contact zone between the product mass and the wall of the boat. Energy dispersive analysis (EDX) showed that the crystals contained the approximate elemental ratio 4Ca:4Co:1Pr:1Al. The lattice parameters and space group as determined from oscillation and Weissen-

berg photographs suggested a phase isostructural with brownmillerite, $\text{Ca}_2\text{Fe}_{2-x}\text{Al}_x\text{O}_5$ (Bertaut, Blum & Sagnieres, 1959; Colville, 1970). The X-ray diffraction data collection and refinement are summarized in Table 1. The lattice constants were obtained from a least-squares calculation using 2θ values from ten reflections in the range $26 < 2\theta < 27^\circ$. For each reflection, eight 2θ values were determined from the permutations of ω , χ , φ , 2θ . Four standard reflections, 341, $\bar{3}41$, 143 and $\bar{1}43$, were measured every 100 min; the random intensity fluctuations did not exceed 2%. E.s.d.'s, $\sigma(F_o)$, were obtained from counting statistics. Absorption corrections were calculated with *ORABS* (Wehe, Busing & Levy, 1962). *SHELX76* (Sheldrick, 1976) was used for the least-squares calculations, direct-methods program, and secondary-extinction correction. The latter was significant for the 200, 002, 080 and 202 reflections varying from almost 22 to 15% of F_c . Atomic scattering factors and corrections for anomalous dispersion were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV).

An E map obtained from the direct-methods calculation yielded cation positions consistent with the brownmillerite structure. The oxygen ion positions were obtained from a Fourier electron density map calculated with phases based on the cation positions. The occupancies of the cations were permitted to vary in the refinement process. The value for Co1 in the octahedral site converged to full occupancy, while for Co2 in the tetrahedral site it was less than one and for Ca greater than one. Al with concentration $(1 - \text{Co}2)$ was then assigned to the tetrahedral cobalt site and Pr with $(1 - \text{Ca})$ concentration was placed into the Ca site. Final atomic coordinates, site occupancies and equivalent isotropic thermal displacement parameters are given in Table 2 and rel-

Table 1. Summary of data collection and structure refinement

Dimensions (mm)	0.19 × 0.16 × 0.02; 0.02 parallel to [010]
Crystal faces	(010), (100), (102), (001)
Diffractometer	Krisel automated Picker
Scan mode; speed (° min ⁻¹); scan width (°)	ω; 4; 1 + 0.35tanθ
Background	2.5 s at high and low ω
h, k, l range	-8 → 8, 0 → 20, -8 → 8
Maximum 2θ (°)	60
Measured reflections	2388
Unique reflections	661
R _{int}	0.019
> 4σ(F)	398
Absorption factor range	5.46-1.25
Number of variables	36
w ⁻¹	σ ² (F _o) + 0.0001F _o ²
S	2.74
Function minimized	Σw(F _o - F _c) ²
R, wR	0.0484, 0.0461
All data: R, wR	0.101, 0.0671
Shift/e.s.d. _{max}	0.001
Δρ _{max,min} (e Å ⁻³)	1.0, -1.4
Extinction parameter, g	3.14 (23) × 10 ⁻⁷
F' = F _c [1 - (gF _c ²)(sinθ) ⁻¹]	

evant bond distances and angles in Table 3.* The thermal displacement parameters for Co/Al are very anisotropic with U_{11} more than ten times U_{22} and U_{33} . This may be due to the Co and Al occupying slightly different positions in the tetrahedron. Fig. 1 shows a drawing of the articulations of the Co1 octahedra and Co2 tetrahedra; the Ca—O bonds are omitted (ORTEP; Johnson, 1976).

Related literature. The solid solution series $\text{Ca}_2\text{Fe}_{2-x}\text{Al}_x\text{O}_5$ crystallizes with the brownmillerite structure; the phase $x = 1$ corresponds to the mineral brownmillerite. The end members exist with $x = 0$ and $x \approx 0.67$ (Bertaut *et al.*, 1959; Geller, Grant & Gonser, 1969) although $\text{Ca}_2\text{Al}_2\text{O}_5$ with the brownmillerite structure can be prepared at high pressure (Aggarwal, Gard, Glasser & Biggar, 1972). This structure type does not exist for $\text{Ca}_2\text{Co}_2\text{O}_5$ (Vidya-sagar, Gopalakrishnan & Rao, 1984). Reflections with $h + k + l = 2n + 1$ are very weak in the brownmillerite structure type (Bertaut *et al.*, 1959) and space group *Imma* (No. 74) has been assigned to some compositions. Smith (1962) has shown that in the solid solution $\text{Ca}_2(\text{Fe}_{1-p}\text{Al}_p)_2\text{O}_5$ the space group is *Pnma* when $p = \text{Al}/(\text{Al} + \text{Fe}) < 0.30$ and *Imma* for $p > 0.33$. He discusses the small adjustments in the coordinates that give rise to the space group change. In this structure reflections $h + k + l = 2n + 1$ are generally weak and are responsible for the high value of *R* for all reflections. The assignment of Co^{2+} to

* Lists of structure factors and anisotropic thermal displacement parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53897 (8 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Atomic coordinates, occupancies and equivalent thermal displacement parameters

U_{eq} calculated from $\frac{1}{3}$ of the trace of the orthogonalized U_{ij} tensor.						
	Occupancy	x	y	z	U_{eq} (Å ²)	
Co1	1	0	0	0	0.0086 (4)	
Co2	0.651 (16)	-0.0013 (20)	$\frac{1}{4}$	-0.0607 (4)	0.0362 (9)	
Al	0.349	-0.0013	$\frac{1}{4}$	-0.0607		
Ca	0.821 (4)	0.0002 (6)	0.10851 (6)	0.4802 (2)	0.0102 (3)	
Pr	0.179	0.0002	0.10851	0.4802		
O1	1	0.2459 (22)	-0.0122 (3)	0.265 (2)	0.0055 (10)*	
O2	1	-0.022 (2)	0.1439 (4)	0.0641 (10)	0.0145 (14)*	
O3	1	-0.1036 (16)	$\frac{1}{4}$	0.6282 (17)	0.0109 (17)*	

* Isotropic refinement.

Table 3. Bond distances (Å) and angles (°)

Co1—O2O1	1.957 (10)	Ca/Pr—O1	2.520 (10)
Co1—O2O1	1.870 (10)	Ca/Pr—O1	2.624 (10)
Co1—O2O2	2.190 (6)	Ca/Pr—O1	2.515 (10)
Co2/Al—O2O2	1.736 (6)	Ca/Pr—O1	2.394 (10)
Co2/Al—O3	1.790 (10)	Ca/Pr—O2	2.347 (6)
Co2/Al—O3	2.132 (13)	Ca/Pr—O2	2.818 (10)
O1—O2O1	2.768 (1)	Ca/Pr—O2	2.589 (10)
O1—O2O2	2.645 (1)	Ca/Pr—O3	2.337 (9)
O1—O2	2.804 (10)		
O1—Co1—O1	92.61 (4)	O2—Co2/Al—O3	110.9 (3)
O1—Co1—O2	90.4 (2)	O2—Co2/Al—O3	97.5 (5)
O1—Co1—O2	93.0 (3)	O3—Co2/Al—O3	97.6 (4)
O2—Co2/Al—O2	132.9 (4)		

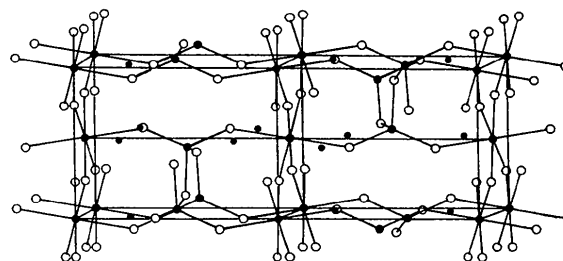


Fig. 1. The brownmillerite-type structure. The vertical axis is *c* and the horizontal axis is *b*. Open circles are oxygen; filled circles are Co1 in octahedral coordination and Co2/Al in tetrahedral coordination. Ca/Pr are shown as non-bonded small filled circles.

the tetrahedral site and Co^{3+} to the octahedral site was made on the basis of site preference (Cotton & Wilkinson, 1988; Wells, 1984). The compound LaSrCuGaO_5 crystallizes with the brownmillerite structure in space group *Ima2* (Vaughney, Wiley & Poepfelmeier, 1990). The brownmillerite structure can be considered an oxygen deficient perovskite and is structurally closely related to other oxygen deficient perovskites, *e.g.* LaSrCuAlO_5 (Wiley, Sabat, Hwu, Poepfelmeier, Reller & Williams, 1990).

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Structure of $[\text{VF}_3(\text{H}_2\text{O})_3]^*$

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Abstract. Triaquatrifluorovanadium(III), $M_r = 161.98$, trigonal, $R3m$, $a = 7.233$ (4), $c = 8.329$ (5) Å, $V = 377.3$ Å³, $Z = 3$, $D_m = 2.10$, $D_x = 2.146$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 18.4$ cm⁻¹, $F(000) = 240$, $T = 293$ K, $R = 0.019$ for 218 unique observed reflections. Discrete complex octahedral molecules $\text{VF}_3(\text{OH}_2)_3$ with an ordered facial arrangement of the two types of ligand and $3m$ symmetry are linked to six other molecules by twelve strong O—H...F hydrogen bonds. As, in the rhombohedral axial setting, $a_R = 5.015$ (3) Å and $\alpha_R = 92.30$ (5)°, the distortion of the V-atom partial structure from the arrangement of lattice points in a primitive cubic lattice is only slight.

Experimental. Green single crystals were obtained by reaction of vanadium powder with 48% hydrofluoric acid at room temperature (Petersen, 1889). The experimental density is quoted from Fischer & Weiss (1964). The crystal used for data collection was a cube of 0.125 mm edge length. Data were collected on a Siemens *AED2* diffractometer with graphite monochromator. The lattice parameters were determined by a least-squares analysis of 30 selected reflections in the range $19 < 2\theta < 35^\circ$ and agreed within the mutual experimental error with those reported earlier (Fischer & Weiss, 1964). Reflection conditions hkl for $-h + k + l = 3n$ proved the R centering. Intensities were measured using a variable

ω - θ scan. Three standard reflections monitored every 2 h were constant within 3%. No corrections for absorption were applied. 1147 reflections were measured with $\sin\theta_{\text{max}}/\lambda < 0.805$ Å⁻¹ in the index range $-11 \leq (h,k) \leq 11$, $0 \leq l \leq 13$. The reflections were averaged to yield 230 independent data, internal $R = 0.037$. Twelve reflections with $I < 1.96\sigma(I)$ were treated as unobserved.

The crystal structure was solved by the heavy-atom method. Least-squares refinement was carried out only with the observed reflections using F magnitudes weighted by $w = [\sigma^2(F)]^{-1}$. The noncentrosymmetric space group had been proved before by piezoelectricity measurements (Fischer & Weiss, 1964). The H atom was located from a difference electron density map. Atomic scattering factors for the neutral atoms and terms for anomalous dispersion were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). Calculations and drawings were performed using the Nicolet *SHELXTL* program system (Sheldrick, 1984) on a Data General Eclipse S/140 computer.

With 19 free parameters, *i.e.* the scale factor, coordinates of all atoms, an isotropic displacement

Table 1. *Atomic coordinates and isotropic displacement parameters with e.s.d.'s in parentheses*

	x	y	z	$U_{\text{eq}}^*/U_{\text{H}}(\text{Å}^2)$
V	0.0	0.0	0.0	0.0176 (1)
F	0.1291 (4)	$2x$	0.1271 (4)	0.034 (1)
O	$2y$	0.1294 (4)	-0.1377 (5)	0.025 (1)
H	0.311 (4)	0.232 (3)	-0.159 (3)	0.047 (7)

$$* U_{\text{eq}} = \frac{1}{3}(U_{11}a^*a^2 + U_{22}b^*c^2 + U_{33}c^*a^2 + \dots)$$

* Part 27 of the series Fluorides and Fluoro Acids. For part 26 see Mootz & Bartmann (1991).

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