$Bi_{2-x}Ca_xIr_2O_{6+y}$ Pyrochlore Phases: Structure and Properties with Varied Ir Oxidation State from 3.9+ to 4.3+

Gabriella Giampaoli[1], Jun Li[1], Arthur P. Ramirez[2], Arthur W. Sleight[1], M.A. Subramanian[1,*]

[1] Department of Chemistry, Oregon State University, Corvallis, OR 97331

[2] Department of Physics, University of California, Santa Cruz, CA 95064, USA

Single Crystal Structure Determination of $Ca_2Ru_2O_7$

Single Crystals of $Ca_2Ru_2O_7$ were grown under low temperature and high pressure conditions. Starting materials, $KRuO_4$ (Aldrich, 99%), and CaO (Aldrich, 99.9%) and 10 ml of water were combined in Teflon lined hydrothermal Parr autoclaves, and heated at 250˚C for 3 days.

Diffraction intensities for $Ca_2Ru_2O_7$ were collected at 173 K on a Bruker Apex2 CCD DUO diffractometer using Cu K_α radiation, λ = 1.5419 Å. The space group was determined based on systematic absences. Absorption correction was applied by SADABS.[S1] The structure was solved by direct methods and Fourier techniques, and refined on F^2 using full matrix least-squares procedures. All calculations were performed by the Bruker SHELXL-2014 package.[S2] The results are summarized in Tables S1 – S3.

The structure of $Ca_2Ru_2O_7$ was previously reported based on a crystal grown hydrothermally, but site occupancies were not refined.[S3] Based on our structure refinement the composition of the crystal is $Ca_{1.7}Ru_2O_7$. This gives an oxidation state for Ru of 5.3+, which is unusually large. The observed Ru–O distance of 1.941 Å is larger than the 1.927 Å value reported for stoichiometric $Cd_2Ru_2O_7$, which suggests that the Ru oxidation state is not higher than 5.0+.[S4] Given the synthesis conditions some O in the O' position may actually be OH, which is frequently found in this position including the mineral pyrochlore $(Na,Ca)_2Nb_2O_6(OH,F)$. We find that "$Ca_{1.7}Ru_2O_7$" decomposes with weight loss on heating in air to 500°C. Thus, $Ca_{1.7}Ru_2O_7$ might actually be more like $Ca_{1.7}Ru_2O_{6.4}(OH)_{0.6}$ with a 5.0+ oxidation state. Whatever the real composition, this structure determination shows that the very large displacements of Ca from the ideal site found in $Bi_{2-x}Ca_xIr_2O_6O'_y$ phases do not occur here where the O' site is fully occupied. More characterization studies are in progress and the results will be included in a future publication.

REFERENCES

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S3. Munenaka, T.; Sato, H. A Novel Pyrochlore Ruthenate: $Ca_2Ru_2O_7$. *J. Phys. Soc. Jap*. **2006**, 75, 103801.

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Table S1. Summary of crystal refinement data for single crystals of $Ca_2Ru_2O_7$.

Structural formula	$Ca_{1.7}Ru_2O_7$
Formula weight	382.27 g/mol
Color and habit	Black, Octahedral
Crystal size (mm^3)	0.01 × 0.01 × 0.01
Space group	$Fd\bar{3}m$
a (Å)	10.187(1)
V ($Å^3$)	1057.1(1)
Z	8
ρ_{calc} (g/cm^3)	4.806
λ (Cu K_α) (Å)	1.5419
μ (mm^{-1})	60.840
θ range for collection (°)	6.53-66.57
Limiting Indices	$-12 \le h \le 12$, $-12 \le k \le 12$, $-11 \le l \le 12$
No. of reflections collected	4076
No. of independent reflections	65
No. of parameters	12
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0217$; $wR_2 = 0.0576$
Final R indices (all data)	$R_1 = 0.0253$; $wR_2 = 0.0608$
Goodness of fit on F^2	1.053
Measurement Temp. (K)	173(2)

Table S2. Single crystal structure information, including thermal parameters and atomic positions.

	Position	x	y	z	U_{11} ($Å^2$) ×10^2	U_{12}=U_{13}=U_{23} ($Å^2$) ×10^2	U_{22}, U_{33} ($Å^2$) ×10^2	U_{iso} ($Å^2$) ×10^2	RMS[a]
Ca	16*c*	0.5	0.5	0.5	2.0(2)	-0.03(7)	U_{11}	2.0(2)	0.14
Ru	16*d*	0	0	0	0.92(8)	-0.04(2)	U_{11}	0.92(8)	0.10
O(1)	8*b*	0.375	0.375	0.375	2.5(3)	0	U_{11}	2.5(3)	0.16
O(2)	48*f*	0.3210(6)	0.125	0.125	2.3(4)	0	1.0(2)	1.5(1)	0.12

a. Root mean square displacement (Å).

Table S3. Comparison of single crystal data to previous work.

	This work	**Ref. S3**
a (Å)	10.187(1)	10.197(2)
x, 1/8, 1/8 (O)	0.3210(6)	0.3219(1)
Ca: U_{11}, U_{12} (Å^2) ×10^2	2.0(2), -0.03(7)	3.2(1)
Ru: U_{11}, U_{12} (Å^2) ×10^2	0.92(8), -0.04(2)	0.81(1)
O: U_{11}, U_{22}=U_{33}, U_{12}=U_{13}=U_{23} (Å^2) ×10^2	2.3(4), 1.0(2), 0	2.0(1)
O': U_{iso} (Å^2) ×10^2	2.5(3)	4.8(1)
A–O (Å) ×6	2.563(4)	2.559
A–O' (Å) ×2	2.206(1)	2.208
Ru–O (Å)	1.941(2)	1.946
Ca RMS[a] (Å)	0.14	0.18
O RMS (Å)	0.12	0.14
O' RMS (Å)	0.16	0.22
Ru RMS (Å)	0.10	0.09
Ca site occupation	0.85(3)	1.0[b]
T (K)	173(2)	300

a. Root mean square displacement.

b. This value was not refined.