Ca^{2+}/vacancies and O^{2-}/F^{-} ordering in new oxyfluoride pyrochlores

$Li_{2x}Ca_{1.5-x}\square_{0.5-x}M_2O_6F$ (M = Nb,Ta) for $0 \leq x \leq 0.5$

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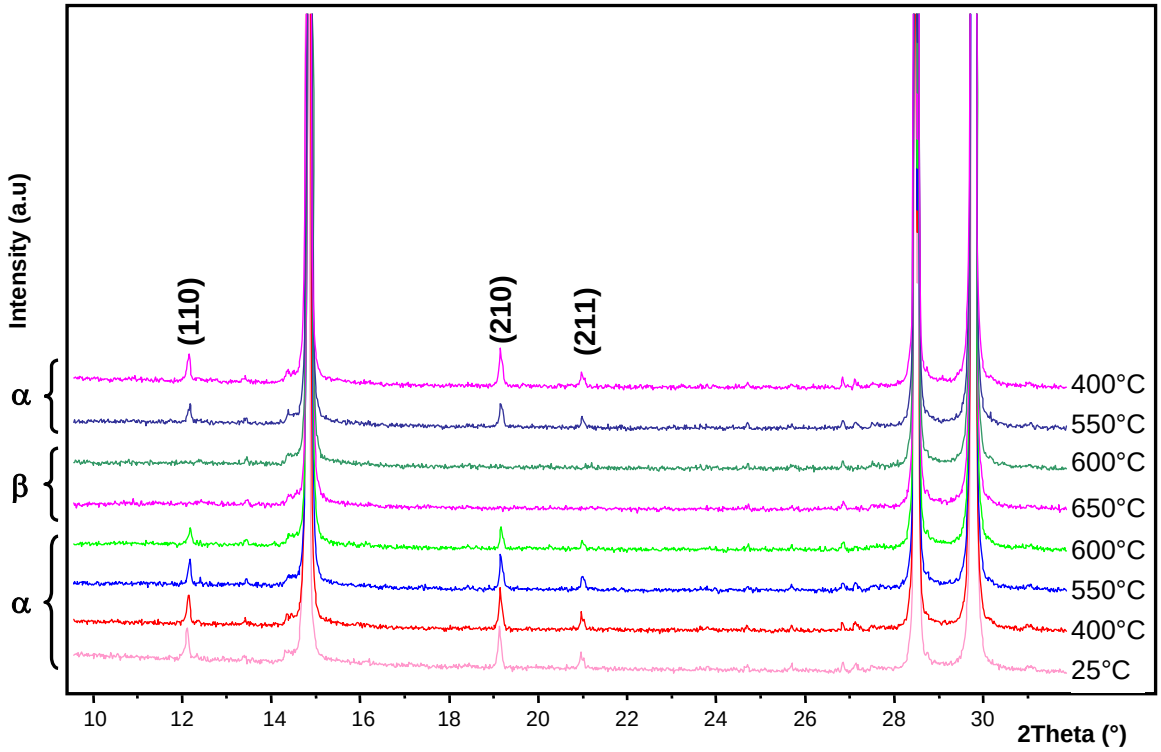
Electronic supplementary information (ESI)



Thermal evolution of $Ca_{1.5}\square_{0.5}Ta_2O_6F$ X-ray powder diffraction patterns showing the α ↔ β transition

Crystallographic parameters and operating conditions of the X-ray data collection and of the refinement for α and β–$Ca_{1.5}\square_{0.5}Nb_2O_6F$

	α-$Ca_{1.5}\square_{0.5}$ Nb_2O_6F	β-$Ca_{1.5}\square_{0.5}$ Nb_2O_6F
Symmetry	Cubic	Cubic
Space Group	$P4_332$ (No. 212) – acentric	$Fd\bar{3}m$ (No. 227)
a= b =c /Å	10.4506(7)	10.444(2)
V /Å^3	1141.4(2)	1139.2(6)
Z	8	8
Formula weight /g	360.92	360.92
Dcalc /gcm^{-3}	4.20	4.21
Temperature /°C	20	20
Radiation /Å	Mo Kα	Mo Kα (graphite monochromatized)
Crystal volume /10^{-4} mm^3	/	13.99
Diffractometer	Bruker-Nonius Kappa CCD	Siemens AED2 four-circle
Scanning mode – aperture /mm		ω/2θ - 4 x 4
Exposure time per frame /s	240	
Range registered :		
2θ max /°	79.97	98
***h, k, l* max**	15, 16, 18	14, 15, 22
Absorption correction	no	Gaussian method
Transmission factors, T_{max}, T_{min}		0.567, 0.763
R_{int}	0.0523	0.0201
Secondary extinction coefficient	0.052(3)	0.0024(2)
Reflections measured		
Total	11758	954
Independent	1109	309
Number of refined parameters	35	11
Weighting scheme	$W = 1/[\sigma^2(F_o^2)+(0.1337 \times P)^2+12.46 \times P]$ where $P = 1/3[Max(F_o^2,0) + 2F_c^2]$	$W = 1/[\sigma^2(F_o^2)+(0.10 \times P)^2]$ where $P = 1/3[Max(F_o^2,0) + 2F_c^2]$
Electron density in final Fourier difference map max, min /e$^-$Å^{-3}	0.75, -3.48	0.96, -0.70
R_1 for data with $F_o > 4\sigma(F_o)$ and for all data	0.0484 (for 934), 0.0619 (for all)	0.0279(for 279 data), 0.0345 (for all)
wR_2	0.1763	0.0689

Anisotropic thermal parameters for α and β-$Ca_{1.5}\square_{0.5}Nb_2O_6F$

	α Form - $P4_332$						β Form - $Fd\bar{3}m$					
	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ca	0.0147(4)	0.0116(3)	0.0116(3)	-0.0028(3)	0.0032(2)	0.0032(2)	0.0186(7)	0.0186(7)	0.0186(7)	-0.0059(7)	-0.0059(7)	-0.0059(7)
Nb1	0.0089(2)	0.0097(2)	0.0097(2)	-0.0021(1)	-0.0006(1)	-0.0006(1)	0.0099(3)	0.0099(3)	0.0099(3)	-0.0012(2)	-0.0012(2)	-0.0012(2)
Nb2	0.0108(2)	0.0108(2)	0.0108(2)	-0.0016(1)	-0.0016(1)	-0.0016(1)						
O1	0.0088(9)	0.006(1)	0.010(1)	-0.0038(7)	0.0007(7)	0.0008(7)	0.014(2)	0.012(2)	0.012(2)	0.007(2)	/	/0
O2	0.0092(9)	0.006(1)	0.011(2)	0.0021(7)	-0.0004(7)	0.0006(8)						
F	0.0124(7)	0.012(1)	0.012(1)	0.0021(7)	0.0021(7)	0.0021(7)	0.021(3)	0.021(3)	0.021(3)	/	/	/

Conditions of X-ray data collection and crystallographic characteristics of α and β–$Ca_{1.5}\square_{0.5}Ta_2O_6F$

	α–$Ca_{1.5}\square_{0.5}Ta_2O_6F$	**β–$Ca_{1.5}\square_{0.5}Ta_2O_6F$**
Diffractometer	X'pert MPD-PRO	
Radiation	CuKα, 40kV, 35mA	
Divergence, antiscattering slits [°]	0.50	
Receiving slit [°]	0.25	
Angular range [°2θ]	5-130	
Step scan increment [°2θ]	0.017	
Count time [sec/step	210	
Miscellaneous	room temperature, sample rotation (16 rpm)	
Space group	$P4_332$ (No.212)	$Fd\bar{3}m$ (No.227)
Cell parameters [Å]	A = 10.43210(9)	a = 10.4331(1)
Volume / Z	1135.3 (9) / Z = 4	1135.64(1)$Å^3$ / Z = 4
Number of reflections	234	65
Number of refined parameters	27	16
Halfwidth parameters	U = 0.0091(6), V = -0.0047(6), W = 0.0040(2)	U = 0.0055(7), V = -0.0024(9), W = 0.0061(3)
Peak shape	Pseudo-Voigt 0.58(2)	Pseudo-Voigt 0.38(3)
Zero point [°2θ]	0.2462(6)	0.2316(9)
Asymmetry parameters	P1 = -0.103(6), P2 = 0.023(2)	P1 = -0.019(8), P2 = 0.013(2)
Reliability factors	R_p = 9.70, R_{wp} = 9.59, χ^2 = 4.73, R_{Bragg} = 2.49	R_p = 7.53, R_{wp} = 8.10, χ^2 = 6.55, R_{Bragg} = 2.20

R_p and R_{wp} are conventional Rietveld values calculated after background substraction.

Anisotropic thermal parameters for α and β–$Ca_{1.5}\square_{0.5}Ta_2O_6F$

	Form α - $P4_332$						Form β - $Fd\bar{3}m$					
	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ta1	-2(9)	6(6)	6(6)	-6(2)	-6(2)	12(9)	10(1)	10(1)	10(1)	0.3(4)	0.3(4)	0.3(4)
Ta2	5(5)	5(5)	5(5)	2(9)	2(9)	2(9)						