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Revealing the peculiar local behavior of manganese and cobalt in diffusion-doped calcium orthovanadate $Ca_3(VO_4)_2$

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Supporting Information

Table S1. Crystallographic data, experimental details and parameters of undoped and diffusion-doped $Ca_3(VO_4)_2$:Mn_2O_3 and $Ca_3(VO_4)_2$:Co_3O_4 crystal structure refinement according to the single-crystal X-ray diffraction (D) and single-crystal synchrotron X-ray diffraction (S).

Method	D			S		
Nominal composition	$Ca_3(VO_4)_2$ [6]	$Ca_3(VO_4)_2$:Mn_2O_3	$Ca_3(VO_4)_2$:Co_3O_4	$Ca_3(VO_4)_2$	$Ca_3(VO_4)_2$:Mn_2O_3	$Ca_3(VO_4)_2$:Co_3O_4
System, Space group, *Z*	Trigonal, *R*3*c*, 21					
a, Å	10.8059(3)	10.7989(3)	10.7827(3)	10.8117(2)	10.6320(2)	10.7790(2)
c, Å	38.0222(15)	37.9041(18)	37.9785(12)	38.0203(13)	37.3860(13)	37.9060(13)
V, Å^3	3844.90	3828.03	3824.05	3848.88	3659.90	3814.13
D_x, g/cm^3	3.175	3.209	3.321	3.169	3.366	3.321
Radiation λ, Å	Mo*K*α, 0.71073			0.79272	0.75312	0.75320
Absorption μ, mm^{-1}	4.65	4.72	5.21	6.34	6.78	7.13
T, K	295(2)			100(1)		
Sample size, mm	~ 0.2 × 0.2 × 0.2			~0.05 × 0.05 × 0.05		
Diffractometer	STOE STADI VARI Platus-100 K			"Belok/XSA" beamline (NRC "Kurchatov institute")		
Type of scan	ω			ϕ		
$2\theta_{max}$, deg	71.87	67.21	62.25	61.99	63.74	61.81
Limits *h, k, l*	$-17 \le h \le 17$, $-11 \le k \le 17$, $-62 \le l \le 59$	$-16 \le h \le 16$, $-15 \le k \le 16$, $-58 \le l \le 58$	$-15 \le h \le 15$, $-11 \le k \le 15$, $-53 \le l \le 54$	$-13 \le h \le 13$, $-14 \le k \le 14$, $-49 \le l \le 49$	$-14 \le h \le 10$, $-14 \le k \le 14$, $-52 \le l \le 50$	$-13 \le h \le 13$, $-13 \le k \le 13$, $-48 \le l \le 48$
No. of reflections: measured/unique ($I > 2\sigma(I)$)	3898/2975	30566/3348	26670/2708	10569/1953	7278/2229	20560/1906

No. of parameters in refinement	146	143	151	148	153	
Weighting scheme	$1/[\sigma^2(F_0^2) + (0.0063P)^2]$,	$1/[\sigma^2(F_0^2) + (0.0122P)^2]$,	$1/[\sigma^2(F_0^2) + (0.0382P)^2]$,	$1/[\sigma^2(F_0^2) + (0.0494P)^2 + 19.61P]$	$1/[\sigma^2(F_0^2) + (0.0932P)^2 + 72.04P]$	$1/[\sigma^2(F_0^2) + (0.0506P)^2 + 19.09P]$
	$P = (F_0^2 + 2F_c^2)/3$					
R_1 ($I > 2\sigma(I)$)	0.0355	0.0481	0.0379	0.0313	0.0448	0.0339
wR_2	0.0472	0.0724	0.0871	0.0837	0.1566	0.0876
S	0.858	0.816	0.960	1.105	1.093	1.022

Table S2. Coordinates of atoms, displacement parameters $U_{eq} \times 10^2$ (Å^2), and site occupancies p (SOF) in the structures of undoped and Mn- and Co-doped $Ca_3(VO_4)_2$ crystals according to the single-crystal X-ray diffraction (D) and single-crystal synchrotron X-ray diffraction (S)

Method	D			S		
Sample/ Parameter	$Ca_3(VO_4)_2$ [6]	$Ca_3(VO_4)_2$:Mn_2O_3	$Ca_3(VO_4)_2$:Co_3O_4	$Ca_3(VO_4)_2$	$Ca_3(VO_4)_2$:Mn_2O_3	$Ca_3(VO_4)_2$:Co_3O_4
Ca1 (*18b*, 1)						
x	0.72979(3)	0.2704(2)	0.2703(2)	0.1473(2)	0.1474(3)	0.1479(2)
y	0.85277(3)	0.1477(2)	0.1476(1)	0.2702(2)	0.2702(3)	0.2706(2)

z	0.05702(2)	0.94200(5)	0.94310(4)	0.55705(4)	0.55688(7)	0.55695(4)
p	1.0	1.0	1.0	1.0	1.0	1.0
U_{eq}	2.542(7)	2.54(4)	2.39(3)	3.29(4)	2.52(5)	2.71(4)
Ca2/Mn2/Co2 (*18b*, 1)						
x	0.72597(3)	0.2739(2)	0.2741(1)	–0.1960(1)	-0.1965(2)	-0.1965(1)
y	0.86262(3)	0.1372(2)	0.1375(1)	0.1964(1)	0.1964(2)	0.1965(1)
z	0.16360(2)	0.83540(4)	0.83625(3)	0.49694(3)	0.49695(6)	0.49712(4)
p(Ca2)	1.0	1.0	1.0	1.0	0.900(5)	0.940(22)
p(Mn2/Co2)					0.100(5)	0.060(22)
U_{eq}	1.654(6)	1.68(4)	1.57(3)	2.31(3)	1.89(6)	2.05(5)
Ca3/Mn3/Co3 (*18b*, 1)						
x	0.61303(3)	0.3868(2)	0.3868(1)	0.5108(1)	0.5107(2)	0.5103(1)
y	0.82217(3)	0.1776(2)	0.1775(1)	0.4571(1)	0.4568(2)	0.4565(1)
z	0.96589(2)	0.03325(5)	0.03433(3)	0.63272(3)	0.63250(5)	0.63247(3)
p(Ca3)	1.0	0.971(9)	0.8850(4)	1.0	0.892(4)	0.951(19)
p(Mn3/Co3)		0.029(9)	0.1150(4)		0.108(4)	0.049(19)
U_{eq}	1.500(6)	1.44(4)	1.65(3)	2.13(3)	1.78(6)	1.85(4)

Ca4/Mn4/Co4 (*6a*, 3)						
x	0	0	0	2/3	2/3	2/3
y	0	0	0	1/3	1/3	1/3
z	0.73426(2)	0.2649(1)	0.26562(6)	0.56746(7)	0.5678(1)	0.56784(6)
p(Ca4)	0.33333	0.306(3)	0.3130(2)	0.33333	0.291(24)	0.281(10)
p(Mn4/Co4)		0.028(3)	0.0200(2)		0.042(24)	0.052
U_{eq}	2.027(9)	2.00(8)	1.46(4)	2.56(4)	2.04(9)	2.18(7)
Ca5/Mn5 (*18b*, 1)						
x	0.9503(3)	0.939(1)	0.053(1)	–0.013(2)	-0.016(1)	-0.014(1)
y	0.9308(3)	0.985(2)	0.070(1)	–0.056(2)	-0.069(2)	-0.064(1)
z	0.92216(7)	0.0769(5)	0.0786(4)	0.4209(3)	0.4218(4)	0.4223(2)
p(Ca5)	0.14636	0.150(9)	0.167(6)	0.147(8)	0.172(12)	0.178(8)
p(Mn5)	-	0.017(9)	-	-	-	-
U_{eq}	4.39(7)	3.93(8)	5.9(3)	4.4(3)	3.8(5)	4.3(3)
Ca5*A* (*6a*, 3)						
x	0			0		
y	0			0		

z	0.9190(1)			0.427(5)		
p	0.05051			0.011(6) [a]		
U_{eq}	4.39(7)			4.4(3)		
V1 (*18b*, 1)						
x	0.68951(2)	0.3103(2)	0.3102(1)	0.4711(1)	0.4705(2)	0.4707(1)
y	0.86258(2)	0.1374(2)	0.1374(1)	0.4934(1)	0.4930(2)	0.4929(1)
z	0.86751(2)	0.13153(4)	0.13245(3)	0.53407(3)	0.53425(5)	0.53428(3)
p	1.0	1.0	1.0	1.0	1.0	1.0
U_{eq}	1.815(5)	1.85(4)	1.65(3)	2.52(3)	2.12(5)	2.18(4)
V2 (*18b*, 1)						
x	0.65050(2)	0.3496(1)	0.3490(1)	0.8172(1)	0.8166(2)	0.8165(1)
y	0.84949(2)	0.1503(2)	0.1499(1)	0.6826(1)	0.6828(2)	0.6828(1)
z	0.76527(2)	0.23382(4)	0.23492(3)	0.59856(3)	0.59863(4)	0.59851(3)
p	1.0	0.988(6)	1.0	1.0	1.0	0.998(9) [a]
U_{eq}	1.220(5)	1.10(4)	1.13(2)	1.93(2)	1.51(4)	1.64(4)
V3 (*6a*, 3)						
x	0	0	0	0	0	0

y	0	0	0	0	0	0
z	0.99997(2)	0.99914(6)	0.00008(4)	0.50002(5)	0.49977(8)	0.49993(5)
p	0.33333	0.330(6) [a]	0.3333	0.33333	0.326(8)	0.333(5) [a]
U_{eq}	1.240(7)	1.25(5)	1.19(4)	1.93(4)	1.4(1)	1.61(7)
O1 (*18b*, 1)						
x	0.7263(2)	0.274(1)	0.2669(8)	0.414(1)	0.411(2)	0.410(1)
y	0.9208(1)	0.079(1)	0.0753(7)	0.4715(9)	0.470(1)	0.4694(8)
z	0.90956(3)	0.0898(2)	0.0904(2)	0.5760(2)	0.5769(3)	0.5761(2)
p	1.0	1.0	1.0	1.0	1.0	1.0
U_{eq}	6.65(5)	6.3(3)	6.1(2)	7.6(3)	5.8(4)	5.9(2)
O2 (*18b*, 1)						
x	0.7716(1)	0.2280(9)	0.2266(5)	0.5619(7)	0.564(1)	0.5632(7)
y	0.7726(1)	0.2253(9)	0.2263(5)	0.6656(6)	0.6672(9)	0.6657(6)
z	0.85424(3)	0.1447(2)	0.1453(1)	0.5211(2)	0.5209(3)	0.5210(2)
p	1.0	1.0	1.0	1.0	1.0	1.0
U_{eq}	3.93(3)	3.4(2)	3.6(1)	4.2(1)	3.5(2)	3.5(1)
O3 (*18b*, 1)						

x	0.72092(9)	0.2791(6)	0.2780(4)	0.3217(5)	0.3215(8)	0.3226(5)
y	0.01174(9)	0.9889(6)	0.9876(4)	0.3757(5)	0.3752(8)	0.3755(5)
z	0.84407(2)	0.1552(2)	0.1561(1)	0.5110(1)	0.5106(2)	0.5106(1)
p	1.0	1.0	1.0	1.0	1.0	1.0
U_{eq}	1.51(2)	1.7(1)	1.42(9)	2.21(8)	1.6(1)	1.76(8)
O4 (*18b*, 1)						
x	0.5090(1)	0.4872(8)	0.4887(6)	0.5844(7)	0.585(1)	0.5846(7)
y	0.7482(1)	0.2496(9)	0.2507(6)	0.4275(7)	0.426(1)	0.4268(7)
z	0.85951(4)	0.1384(3)	0.1391(2)	0.5265(2)	0.5262(4)	0.5266(3)
p	1.0	1.0	1.0	1.0	1.0	1.0
U_{eq}	4.99(4)	5.1(3)	5.1(2)	5.7(2)	4.5(3)	4.9(2)
O5 (*18b*, 1)						
x	0.6279(1)	0.3738(8)	0.3738(5)	0.8470(7)	0.847(1)	0.8469(7)
y	0.8205(1)	0.1810(8)	0.1809(5)	0.7064(7)	0.708(1)	0.7075(7)
z	0.72142(2)	0.2775(2)	0.2788(1)	0.5548(2)	0.5543(3)	0.5545(2)
p	1.0	1.0	1.0	1.0	1.0	1.0
U_{eq}	2.98(3)	2.8(1)	2.8(1)	3.6(1)	2.9(2)	3.0(1)

O6 (*18b*, 1)						
x	0.5954(1)	0.4043(8)	0.4039(5)	0.7006(7)	0.699(1)	0.6992(7)
y	0.9657(1)	0.0335(8)	0.0316(5)	0.7383(6)	0.738(1)	0.7376(6)
z	0.77539(3)	0.2236(2)	0.2250(1)	0.6088(1)	0.6090(2)	0.6087(1)
p	1.0	1.0	1.0	1.0	1.0	1.0
U_{eq}	3.49(3)	3.2(2)	2.9(1)	4.0(1)	3.5(2)	3.6(1)
O7 (*18b*, 1)						
x	0.5658(2)	0.435(1)	0.4311(7)	0.9803(8)	0.982(1)	0.9808(8)
y	0.6851(1)	0.3117(9)	0.3126(6)	0.7658(8)	0.766(1)	0.7661(7)
z	0.78368(4)	0.2141(3)	0.2153(2)	0.6174(2)	0.6171(3)	0.6172(2)
p	1.0	1.0	1.0	1.0	1.0	1.0
U_{eq}	5.33(5)	5.7(3)	4.8(2)	5.7(2)	4.4(3)	5.0(2)
O8 (*18b*, 1)						
x	0.82562(8)	0.1738(6)	0.1737(4)	0.7430(5)	0.7430(8)	0.7426(5)
y	0.9240(1)	0.0764(8)	0.0751(4)	0.5077(5)	0.5076(8)	0.5064(5)
z	0.77725(2)	0.2219(2)	0.2234(1)	0.6104(1)	0.6105(2)	0.6100(1)
p	1.0	1.0	1.0	1.0	1.0	1.0

U_{eq}	1.61(2)	1.7(1)	1.55(9)	2.48(9)	1.9(1)	2.26(9)
O9 (*6a*, 3)						
x	0	0	0	0	0	0
y	0	0	0	0	0	0
z	0.04396(5)	0.9552(4)	0.9560(2)	0.5440(3)	0.5443(4)	0.5437(3)
p	0.33333	0.33333	0.33333	0.33333	0.33333	0.33333
U_{eq}	4.35(6)	3.6(3)	4.0(3)	5.3(3)	3.7(4)	4.2(3)
O10 (*18b*, 1)						
x	0.0092(1)	0.9901(9)	0.9905(6)	0.1453(6)	0.1462(9)	0.1459(5)
y	0.8539(1)	0.1445(7)	0.1456(5)	–0.0104(6)	-0.0094(9)	-0.0092(6)
z	0.98707(4)	0.0120(3)	0.0130(2)	0.4873(2)	0.4872(3)	0.4870(2)
p	1.0	1.0	1.0	1.0	1.0	1.0
U_{eq}	3.45(3)	3.2(2)	3.2(1)	3.9(1)	3.1(2)	3.2(1)

[a] taking into account 3σ, the site is defect-free.

Table S3. Main interatomic distances *d* (Å) in the structures of undoped and Mn- and Co-doped $Ca_3(VO_4)_2$ crystals according to the single-crystal X-ray diffraction (D) and single-crystal synchrotron X-ray diffraction (S)

Method	D			S		
Sample/ Parameter	$Ca_3(VO_4)_2$ [6]	$Ca_3(VO_4)_2$:Mn_2O_3	$Ca_3(VO_4)_2$:Co_3O_4	$Ca_3(VO_4)_2$	$Ca_3(VO_4)_2$:Mn_2O_3	$Ca_3(VO_4)_2$:Co_3O_4
Ca1 – O6	2.398(1)	2.397(7)	2.388(5)	2.399(5)	2.370(9)	2.394(5)
– O3	2.408(1)	2.411(7)	2.401(5)	2.403(5)	2.368(7)	2.405(5)
– O2	2.503(1)	2.515(7)	2.488(6)	2.498(6)	2.443(9)	2.487(5)
– O9	2.580(1)	2.581(3)	2.574(2)	2.582(3)	2.535(4)	2.579(3)
– O5	2.594(1)	2.575(8)	2.572(5)	2.586(7)	2.539(10)	2.578(6)
– O7	2.642(1)	2.689(9)	2.685(7)	2.660(8)	2.605(12)	2.646(8)
– O1	2.694(2)	2.686(9)	2.669(7)	2.699(9)	2.637(15)	2.654(9)
– O5	2.713(2)	2.713(7)	2.706(6)	2.713(6)	2.661(9)	2.699(6)
$[Ca1–O]_{av}$	2.567	2.571	2.560	2.568	2.520	2.555
Ca2/Mn2/Co2 – O7	2.298(1)	2.275(9)	2.285(6)	2.298(7)	2.258(11)	2.297(7)
– O5	2.383(1)	2.385(7)	2.372(5)	2.388(6)	2.335(11)	2.370(7)
– O6	2.428(1)	2.421(8)	2.442(5)	2.422(6)	2.376(9)	2.425(6)

– O4	2.448(2)	2.473(9)	2.468(7)	2.461(7)	2.417(11)	2.451(7)
– O3	2.477(1)	2.473(7)	2.480(5)	2.475(5)	2.426(7)	2.455(4)
– O10	2.499(1)	2.513(8)	2.499(5)	2.508(6)	2.461(9)	2.500(6)
– O4	2.573(2)	2.588(9)	2.593(7)	2.576(8)	2.515(12)	2.560(8)
$[Ca2/Mn2/Co2–O]_{av}$	2.444	2.447	2.448	2.447	2.398	2.437
Ca3/Mn3/Co3 – O3	2.350(1)	2.346(6)	2.342(4)	2.356(5)	2.314(7)	2.357(5)
– O10	2.382(2)	2.384(8)	2.378(6)	2.378(5)	2.345(8)	2.376(5)
– O2	2.400(1)	2.408(8)	2.414(6)	2.399(6)	2.353(10)	2.395(6)
– O8	2.428(1)	2.433(8)	2.424(5)	2.439(5)	2.395(8)	2.437(5)
– O1	2.432(1)	2.430(9)	2.449(6)	2.439(8)	2.372(12)	2.431(8)
– O8	2.456(1)	2.447(8)	2.463(5)	2.455(5)	2.408(7)	2.442(5)
– O6	2.828(1)	2.820(8)	2.815(5)	2.836(6)	2.781(10)	2.823(6)
– O7	2.901(2)	2.910(9)	2.861(7)	2.885(8)	2.832(12)	2.871(8)
$[Ca3/Mn3/Co3–O]_{av}$	2.522	2.522	2.518	2.523	2.475	2.517
Ca4/Mn4/Co4 – 3 × O4	2.277(1)	2.268(8)	2.256(6)	2.272(7)	2.237(11)	2.265(7)
– 3 × O8	2.313(1)	2.304(7)	2.284(5)	2.312(5)	2.265(9)	2.276(5)
$[Ca4/Mn4/Co4–O]_{av}$	2.295	2.286	2.270	2.292	2.251	2.271

Ca5/Mn5 – O1	2.416(4)	2.41(2)	2.32(2)	2.43(2)	2.35(2)	2.40(1)
– O1	2.427(4)	2.47(2)	2.38(2)	2.50(2)	2.42(2)	2.48(2)
– O10	2.778(3)	2.79(2)	2.81(2)	2.86(1)	2.762(18)	2.79(1)
– O10	2.925(3)	2.89(2)	2.92(2)	2.95(1)	2.874(18)	2.89(1)
$[Ca5/Mn5–O]_{av}$	2.637	2.64	2.61	2.69	2.602	2.64
Ca5*A* – 3 × O1	2.660(2)	2.66(1)	2.603(9)	2.74(5)	2.61(2)	2.46(15)
– 3 × O10	3.059(4)	3.04(6)	3.00(2)	2.8(1)	3.00(2)	2.86(8)
$[Ca5A–O]_{av}$	2.860	2.85	2.802	2.77	2.81	2.66
V1 – O2	1.688(1)	1.669(7)	1.684(6)	1.688(6)	1.682(9)	1.691(6)
– O1	1.691(1)	1.675(9)	1.704(6)	1.682(7)	1.685(12)	1.683(7)
– O3	1.721(1)	1.717(6)	1.725(5)	1.716(5)	1.697(7)	1.714(5)
– O4	1.736(1)	1.694(8)	1.705(6)	1.722(8)	1.715(12)	1.725(8)
$[V1-O]_{av}$	1.709	1.689	1.705	1.702	1.695	1.703
V2 – O6	1.681(1)	1.684(7)	1.695(5)	1.692(6)	1.666(9)	1.686(6)
– O7	1.690(1)	1.685(9)	1.692(6)	1.687(7)	1.673(11)	1.690(7)
– O5	1.691(1)	1.684(7)	1.695(5)	1.689(6)	1.685(9)	1.695(6)
– O8	1.707(1)	1.712(6)	1.700(4)	1.704(5)	1.680(8)	1.711(5)

$[V2–O]_{av}$	1.692	1.691	1.696	1.693	1.676	1.696
V3 – O9	1.673(2)	1.67(1)	1.675(9)	1.67(1)	1.664(17)	1.66(1)
– 3 × O10	1.703(1)	1.688(6)	1.696(5)	1.701(5)	1.673(7)	1.697(5)
$[V3–O]_{av}$	1.696	1.684	1.691	1.693	1.671	1.688

Table S4. Crystallographic data, experimental details and parameters of diffusion-doped $Ca_3(VO_4)_2$:Mn_2O_3 and $Ca_3(VO_4)_2$:Co_3O_4 crystal structure refinement according to the synchrotron X-ray powder diffraction (P).

Sample/Parameter	$Ca_3(VO_4)_2$:Mn_2O_3	$Ca_3(VO_4)_2$:Co_3O_4
Space group	*R*3*c*	
a, Å	10.81176(8)	10.80154(11)
c, Å	38.0173(3)	37.9672(5)
V, Å^3	3848.62(5)	3836.28(8)
Scherrer size, nm	164.3	631.5
Microstrains, %	0.14	0.25
Admixture phase	-	CoO, 5.6%
R_p	1.39	3.56
wR_p	1.84	4.85
R_{Bragg}	2.32	5.10

Table S5. Coordinates of atoms, displacement parameters $U_{eq} \times 10^2$ (Å^2), and site occupancies p (SOF) in the structures of Mn- and Co-doped $Ca_3(VO_4)_2$ crystals according to powder synchrotron X-ray diffraction (P)

Sample/Parameter	$Ca_3(VO_4)_2$:Mn_2O_3	$Ca_3(VO_4)_2$:Co_3O_4	Sample/Parameter	$Ca_3(VO_4)_2$:Mn_2O_3	$Ca_3(VO_4)_2$:Co_3O_4
Ca1			**O1**		
x	0.2683(2)	0.2671(3)	x	0.2724(7)	0.2671(12)
y	0.1482(2)	0.1518(4)	y	0.0763(6)	0.0722(11)
z	0.9465(7)	0.9457(4)	z	0.0958(7)	0.0947(3)
p	1.0	1.0	p	1.0	1.0
U_{eq}	2.72(5)	0.37(4)	U_{eq}	4.9(2)	2.5(4)
Ca2/Co2			**O2**		
x	0.2711(3)	0.2747(3)	x	0.2274(9)	0.2206(18)
y	0.1359(3)	0.1433(5)	y	0.2236(8)	0.2237(17)
z	0.8401(7)	0.8391(4)	z	0.1466(7)	0.1457(5)
p(Ca2)	1.0	0.917(11)	p	1.0	1.0
p(Co2)		0.083(11)	U_{eq}	4.1(2)	5.4(5)
U_{eq}	2.01(6)	2.19(9)			
Ca3/Mn3			**O3**		

x	0.3876(2)	0.3885(4)	*x*	0.2824(7)	0.2866(13)
y	0.1788(3)	0.1814(6)	*y*	-0.0095(6)	-0.0053(12)
z	0.0376(7)	0.0371(4)	*z*	0.1604(7)	0.1584(4)
p(Ca3)	0.938(8)	1.0	*p*	1.0	1.0
p(Mn3)	0.062(8)		U_{eq}	0.27(17)	0.2(3)
U_{eq}	1.44(6)	1.61(9)			
Ca4/Mn4/Co4			**O4**		
x	0	0	*x*	0.4807(6)	0.4879(11)
y	0	0	*y*	0.2470(9)	0.2484(17)
z	0.2687(7)	0.2684(4)	*z*	0.1410(7)	0.1402(6)
p(Ca4)	0.893(11)	0.812(14)	*p*	1.0	1.0
p(Mn4/Co4)	0.107(11)	0.188(14)	U_{eq}	5.5(2)	4.3(4)
U_{eq}	0.88(8)	1.11(12)			
Ca5			**O5**		
x	0.057(2)	-0.020(7)	*x*	0.3694(5)	0.3684(11)
y	0.0858(15)	0.037(6)	*y*	0.1750(7)	0.1755(16)
z	0.0832(10)	0.0816(12)	*z*	0.2821(7)	0.2812(5)

p	0.118(11)	0.114(2)	*p*	1.0	1.0
U_{eq}	3.4(5)	4.3(9)	U_{eq}	3.6(2)	3.9(4)
Ca5*A*			**O6**		
x	0	0	*x*	0.4054(6)	0.3984(11)
y	0	0	*y*	0.0369(6)	0.0332(9)
z	0.0765(5)	0.0844(19)	*z*	0.2270(7)	0.2244(5)
p	0.194(10)	0.168(6)	*p*	1.0	1.0
U_{eq}	3.4(5)	2.4(9)	U_{eq}	1.8(2)	1.80(17)
V1			**O7**		
x	0.3101(2)	0.3113(3)	*x*	0.4392(9)	0.4445(14)
y	0.1385(2)	0.1423(4)	*y*	0.3190(8)	0.3197(13)
z	0.1361(7)	0.1356(4)	*z*	0.2186(6)	0.2193(5)
p	1.0	1.0	*p*	1.0	1.0
U_{eq}	1.53(5)	1.73(10)	U_{eq}	4.0(2)	1.8(4)
V2			**O8**		
x	0.3487(2)	0.3479(4)	*x*	0.1686(5)	0.1704(9)
y	0.1486(2)	0.1497(4)	*y*	0.0771(7)	0.0652(9)

z	0.2384(7)	0.2379(4)	*z*	0.2254(7)	0.2224(4)
p	1.0	1.0	*p*	1.0	1.0
U_{eq}	1.28(5)	0.92(8)	U_{eq}	0.7(1)	1.0(2)
V3			**O9**		
x	0	0	*x*	0	0
y	0	0	*y*	0	0
z	0.0038(7)	0.0033(4)	*z*	0.9570(6)	0.9590(8)
p	0.33333	0.33333	*p*	0.33333	0.33333
U_{eq}	1.21(8)	0.23(12)	U_{eq}	1.5(2)	4.7(7)
			O10		
			x	-0.0079(7)	-0.0001(15)
			y	0.1414(5)	0.1485(11)
			z	0.0160(7)	0.0157(4)
			p	1.0	1.0
			U_{eq}	1.9(2)	2.5(4)

Table S6. Main interatomic distances *d* (Å) in the structures of undoped and Mn- and Co-doped $Ca_3(VO_4)_2$ crystals according to powder synchrotron X-ray diffraction (P)

Sample/Parameter	$Ca_3(VO_4)_2$:Mn_2O_3	$Ca_3(VO_4)_2$:Co_3O_4
Ca1 – O6	2.45(3)	2.56(2)
– O3	2.44(3)	2.411(18)
– O2	2.50(2)	2.49(2)
– O9	2.548(6)	2.561(7)
– O5	2.61(2)	2.56(2)
– O7	2.65(3)	2.57(2)
– O1	2.65(2)	2.606(11)
– O5	2.71(2)	2.76(2)
$[Ca1–O]_{av}$	2.57	2.56
Ca2/Co2 – O7	2.22(3)	2.24(2)
– O5	2.39(3)	2.37(2)
– O6	2.39(3)	2.39(2)
– O4	2.50(2)	2.49(2)

– O3	2.45(1)	2.47(2)
– O10	2.550(7)	2.56(1)
– O4	2.63(3)	2.648(19)
$[Ca2/Co2–O]_{av}$	2.45	2.45
Ca3/Mn3 – O3	2.34(3)	2.40(2)
– O10	2.44(1)	2.45(1)
– O2	2.50(3)	2.49(3)
– O8	2.40(2)	2.26(1)
– O1	2.51(3)	2.52(2)
– O8	2.44(1)	2.51(1)
– O6	2.82(3)	2.72(2)
– O7	2.94(3)	2.92(2)
$[Ca3/Mn3–O]_{av}$	2.55	2.53
Ca4/Mn4/Co4 – 3 × O4	2.29(2)	2.22(2)
– 3 × O8	2.28(3)	2.37(2)
$[Ca4/Mn4/Co4–O]_{av}$	2.285	2.295

Ca5 – O1	2.33(3)	2.11(9)
– O1	2.44(3)	2.40(5)
– O10	2.79(3)	2.75(4)
– O10	3.01(1)	2.95(4)
$[Ca5–O]_{av}$	2.64	2.55
Ca5*A* –3 × O1	2.73(3)	2.61(2)
– 3 × O10	2.79(3)	2.76(3)
$[Ca5A–O]_{av}$	2.76	2.65
V1 – O2	1.62(1)	1.66(2)
– O1	1.64(3)	1.69(2)
– O3	1.74(2)	1.71(2)
– O4	1.628(7)	1.67(1)
$[V1-O]_{av}$	1.66	1.68
V2 – O6	1.66(1)	1.69(2)
– O7	1.77(2)	1.74(2)
– O5	1.68(4)	1.66(2)
– O8	1.77(1)	1.77(1)

$[V2–O]_{av}$	1.72	1.72
V3 – O9	1.78(3)	1.66(3)
– 3 × O10	1.64(1)	1.58(2)
$[V3–O]_{av}$	1.68	1.60

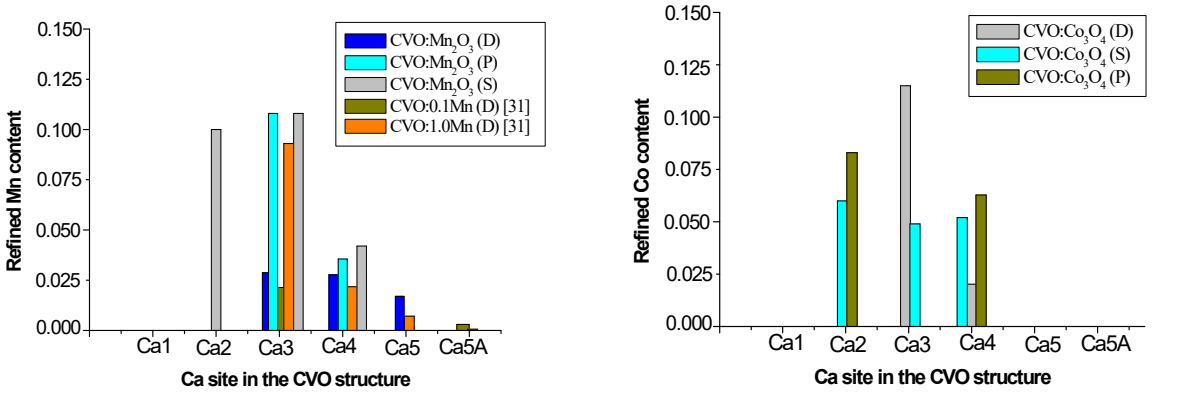

Fig. S1. Refined Mn (*a*) and Co (*b*) content in the Ca crystallographic sites in the Mn- and Co-doped $Ca_3(VO_4)_2$ crystals.

Additional discussion on the local structure of Mn ions in $Ca_3(VO_4)_2$

It should be noted that the formal charge of manganese ions cannot be > 4 since, in this case, a very strong shift towards small values of *R*, Å should be observed in Fig. 6c and that towards large values of *E*, eV in Figs. 6a,b. It is an additional evidence of the absence of Mn^{5+} ions in the structure of CVO:Mn_2O_3. This is in agreement with the general trends of manganese oxides, for which the pre-edge information varies linearly as a function of Mn valence state or symmetry but varies nonlinearly as a function of both parameters [F. Farges, *Physical review B 71*(15) (2005) 155109]. Toriumi et al. [H. Toriumi et al. *Inorganic Chemistry Frontiers 6*(6) (2019) 1587] reported the Mn K-edge EXAFS/XANES data for $Ba_3(MnO_4)_2$ samples with Mn^{5+} ions. The spectra differ significantly from those for CVO:Mn_2O_3 (Fig. 7). Coordination polyhedron MnO_4^{3-} with C_{3v} symmetry (trigonal pyramid) in $Ba_3(MnO_4)_2$ has smaller interatomic distances (Mn–O1 × 3 = 1.702 Å and Mn–O2 × 1 = 1.664 Å [54]) compared to VO_4 polyhedra (symmetry C_1 for V1 and V2, symmetry C_{3v} for V3) in the CVO:Mn_2O_3 structure (see ESI Table S3), which is due to the smaller size of the Mn^{5+} ion compared with the V^{5+} ions. These are another confirmations of not only even partial presence of Mn^{5+} ions in the V^{5+} site, but also the absence of Mn^{5+} ions in the CVO:Mn_2O_3 structure, which is not consistent with the conclusions given in Ref. [I. S. Voronina et al.. *Journal of Crystal Growth 563* (2021) 126104].

Refined actual compositions (see ESI, Table S2), the found distribution of manganese ions over calcium sites (see ESI, Fig. S1), and formal charges of manganese and its local environment in the CVO:Mn [G. M. Kuz'micheva et al. *Materials Research Bulletin 140* (2021) 111300] and CVO:Mn_2O_3 indicates different structural behavior of manganese in these structures depending on the method of dopant introduction. This is due to different synthesis processes and conditions. During Czochralski growth, the formation of CVO melt with a small and limited amount of Mn_2O_3 introduced over CVO stoichiometry (CVO:Mn) occurs [G. M. Kuz'micheva et al. *Materials Research Bulletin 140* (2021) 111300]. A solid-phase high-temperature diffusion annealing implies the contact of CVO crystal with Mn_2O_3 solid phase (CVO:Mn_2O_3), which contributes to the introduction of manganese into the CVO structure under the influence of temperature and concentration gradient. It can be assumed, that in the first method, the pre-crystallization melt contains associates of calcium and manganese. Their coordination environment is similar with that of Ca and Mn atoms in the crystal structure, the Mn^{3+} ions exhibit their crystal-chemical nature. In the second case, during diffusion high-temperature annealing, Mn_2O_3 decomposes to Mn_3O_4 and O_2. Then the particles are adsorbed on the surface of the CVO crystal, followed by their "capture" by free bonds. As a result, a diffusion of tetrahedral groups with manganese ions (the "radius" of the group is ~ 1.3 Å) along the channels (channel size is ~ 5.5 Å) in the framework structure (Fig. 3b, 4b) with their final localization in calcium polyhedra with the

retention of the crystallochemical specificity of $Mn^{(2+\delta)+}$, manifested in the Mn_3O_4 structure, is occured. If manganese atoms (ions) rather than groups with oxygen were involved in diffusion process, the structural analysis would have revealed their location in the positions marked by crosses in Fig. 4.