Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting information

Crystal structure and thermal expansion of novel substitutionally disordered $Ca_{10}TM_{0.5}(VO_4)_7$ (TM=Co, Cu) orthovanadates

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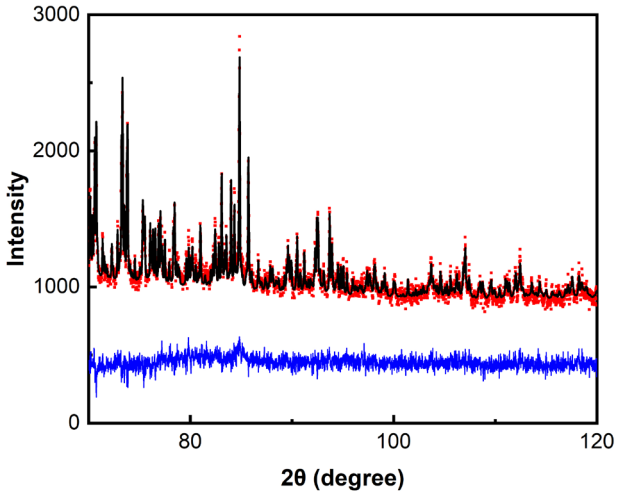

Figure S1-a. Rietveld refinement of $Ca_{10}Co_{0.5}(VO_4)_7$ – angles between 70 and 120 (2θ°).

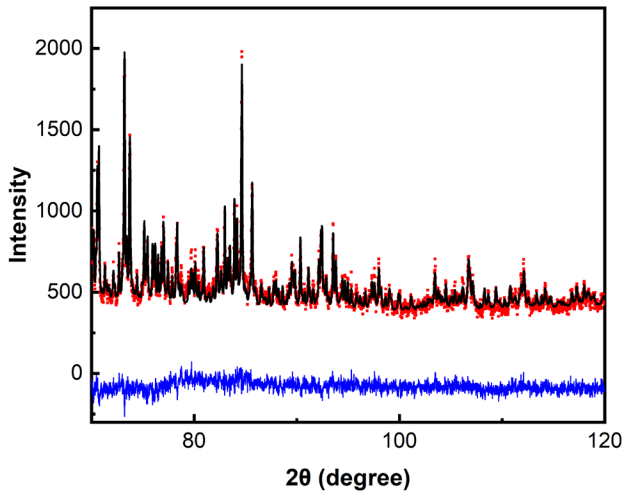

Figure S1-b. Rietveld refinement of $Ca_{10}Cu_{0.5}(VO_4)_7$ – angles between 70 and 120 (2θ°).

Table S1. Dependence of lattice parameters and unit-cell volume on temperature for $Ca_{10}Co_{0.5}(VO_4)_7$ and $Ca_{10}Cu_{0.5}(VO_4)_7$ in the 300–810 K – numerical data of figure 4.

T (K)	$Ca_{10}Co_{0.5}(VO_4)_7$				$Ca_{10}Cu_{0.5}(VO_4)_7$			
	a (Å)	*c* (Å)	*c*/*a*	*V* (Å^3)	*a* (Å)	*c* (Å)	*c*/*a*	*V* (Å^3)
300	10.7814 (3)	37.8230(10)	3.5082(1)	3807.50(16)	10.7876(3)	37.9016(10)	3.5135(1)	3819.74(17)
325	10.7848 (2)	37.8341(9)	3.5081(1)	3810.97(15)	10.7894(3)	37.9068(11)	3.5133(1)	3821.56(18)
379	10.7935 (2)	37.8603(10)	3.5077(1)	3819.76(16)	10.7983(2)	37.9373(10)	3.5133(1)	3830.95(16)
434	10.8018(2)	37.8867(9)	3.5074(1)	3828.30(14)	10.8057(3)	37.9610(11)	3.5130(1)	3838.63(18)
489	10.8104(2)	37.9137(9)	3.5071(1)	3837.18(14)	10.8151(3)	37.9922(10)	3.5129(1)	3848.47(17)
543	10.8192(2)	37.9394(9)	3.5067(1)	3846.04(14)	10.8232(3)	38.0168(13)	3.5125(1)	3856.70(21)
598	10.8286(2)	37.9683(8)	3.5063(1)	3855.66(13)	10.8320(3)	38.0458(11)	3.5124(1)	3865.93(18)
652	10.8373(2)	37.9949(8)	3.5059(1)	3864.56(14)	10.8418(3)	38.0770(10)	3.5120(1)	3876.13(17)
706	10.8462(2)	38.0216(9)	3.5055(1)	3873.61(14)	10.8510(3)	38.1063(10)	3.5118(1)	3885.69(16)
759	10.8552(2)	38.0502(9)	3.5053(1)	3882.93(14)	10.8587(3)	38.1319(12)	3.5116(1)	3893.83(19)
810	10.8645(2)	38.0807(9)	3.5051(1)	3892.70(15)	10.8676(3)	38.1596(10)	3.5113(1)	3903.00(18)

Table S2. Fitted coefficients of equatin *y*=A+B*T*+C/*T* approximting, in the 300-800 K range, the temperature runs of lattice parameters and unit-cell volume for $Ca_{10}Co_{0.5}(VO_4)_7$ and $Ca_{10}Cu_{0.5}(VO_4)_7$

	$Ca_{10}Co_{0.5}(VO_4)_7$				$Ca_{10}Cu_{0.5}(VO_4)_7$			
	a	*c*	*c*/*a*	V	*a*	*c*	*c*/*a*	V
A	10.71695	37.63057	3.51122	3742.1742	10.72361	37.69204	3.51481	3749.3911
B	1.75E-04	5.37E-04	-7.1914E-6	0.17978	1.73E-04	5.60E-04	-4.2376E-6	0.18303
C	3.51139	9.45313	-0.25301	3421.311	3.28548	11.678	0.02022	4425.6472

Table S3. Fitted coefficients of linear equation *y*=A<*r*>+B approximating the lattice parameters and unit-cell volume for whitlockite related materials, as graphically presented in Fig. 6.

	a		*c*		V/V_0
	orthophosphate	orthovanadate	orthophosphate	orthovanadate	
A	0.02763	0.0149	0.01438	0.0289	0.02256
B	0.97235	0.9851	0.98562	0.9711	0.97742

Table S4. Present and reported volume of unsubstituted and substituted orthophosphate and orthovanadate whitlockite related materials with partial or full substitution of Ca at M5 site by divalent transition-metal ions Co, Ni and Cu – numerical data of figure 6-d.

$Ca_{10.5-x}M_x(XO_4)_7$	x	M^{2+}	Volume (Å^3)	reference
$Ca_{10.5-x}M_x(PO_4)_7$	0	-	3527(1)	[1]
	0.35	Ni^{2+}	3489.22(9)	[2]
	0.35	Cu^{2+}	3500.48(7)	[2]
	0.5	Cu^{2+}	3487.1(8)	[3]
	0.5	Cu^{2+}	3485(1)	[4]
	1	Co^{2+}	3449.2(1)	[5]
	1	Cu^{2+}	3463.8(9)	[6]
$Ca_{10.5-x}M_x(VO_4)_7$	0	-	3847(2)	[7]
	0.5	Co^{2+}	3806.67(4)	This work
	0.5	Cu^{2+}	3819.23(4)	This work

References:

1 B. Dickens, L. W. Schroeder and W. E. Brown, *J. Solid State Chem.*, 1974, **10**, 232–248.

2 A. Altomare, R. Rizzi, M. Rossi, A. El Khouri, M. Elaatmani, V. Paterlini, G. Della Ventura and F. Capitelli, *Crystals*, 2019, **9**, 288.

3 A. A. Belik, O. V Yanov and B. I. Lazoryak, *Mater. Res. Bull.*, 2001, **36**, 1863–1871.

4 A. Benarafa, M. Kacimi, G. Coudurier and M. Ziyad, *Appl. Catal. A Gen.*, 2000, **196**, 25–35.

5 A. . Belik, V. . Morozov, S. . Khasanov and B. . Lazoryak, *Mater. Res. Bull.*, 1998, **33**, 987–995.

6 B. I. Lazoryak, N. Khan, V. A. Morozov, A. A. Belik and S. S. Khasanov, *J. Solid State Chem.*, 1999, **145**, 345–355.

7 R. Gopal and C. Calvo, *Z. Krist.*, 1973, **137**, 67–85.