Electronic Supplementary Material (ESI) for CrystEngComm.

Electronic supplementary information

Formation of breathing pyrochlore lattice: structural, thermodynamic and crystal chemical aspects

Mikhail V.Talanov, Valeriy M. Talanov

Let us consider the theoretical derivation of the $F\bar{4}3m$ ordered pyrochlore structure from the disordered $Fd\bar{3}m$ pyrochlore structure $A^{16d}{}_2B^{16c}{}_2X^{48f}{}_6Y^{8b}$. Choose the origin at Wyckoff position 8*a* of $Fd\bar{3}m$ space group. Then the atomic coordinates of the pyrochlore primitive cell (it contain two formula units) in the structures of the disordered and ordered phases are presented in Tables S1-S4.

Table S1. Atom A coordinates at position 16*d* of the pyrochlore structure

Atom number	1	2	3	4
Coordinates of A atoms in the $Fd\bar{3}m$ structure of pyrochlore	5/8, 5/8, 5/8	5/8, 3/8, 3/8	3/8, 5/8, 3/8	3/8, 3/8, 5/8
Vector basis functions (displacements of atoms A)	111	1-1-1	-11-1	-1-11
Coordinates of A atoms in the structure of $F\bar{4}3m$ pyrochlore (in the basis of the structure $Fd\bar{3}m$ of pyrochlore)	$5/8+\delta_A$, $5/8+\delta_A$, $5/8+\delta_A$	$5/8+\delta_A$, $3/8-\delta_A$, $3/8-\delta_A$	$3/8-\delta_A$, $5/8+\delta_A$, $3/8-\delta_A$	$3/8-\delta_A$, $3/8-\delta_A$, $5/8+\delta_A$
Coordinates of A atoms in the structure of $F\bar{4}3m$ pyrochlore (in the basis of the structure $F\bar{4}3m$ pyrochlore)	*x*, *x*, *x*	*x*, -*x*, -*x*	-*x*, *x*, -*x*	-*x*, -*x*, *x*

Atoms A occupy Wyckoff positions 16*e* (x, x ,x), where $x = 5/8+\delta_A = 0.625+\delta_A$ in the structure of ordered $F\bar{4}3m$ pyrochlore

Table S2. Atom B coordinates at position 16*c* of the pyrochlore structure

Atom number	1	2	3	4
Coordinates of B atoms in the $Fd\bar{3}m$ structure of pyrochlore	1/8, 1/8, 1/8	1/8, 3/8, 3/8	3/8, 1/8, 3/8	3/8, 3/8, 1/8
Vector basis functions (displacements of atoms B)	111	1-1-1	-11-1	-1-11
Coordinates of B atoms in the structure of $F\bar{4}3m$ pyrochlore (in the basis of the structure $Fd\bar{3}m$ of pyrochlore)	$1/8+\delta_B$, $1/8+\delta_B$, $1/8+\delta_B$	$1/8+\delta_B$, $3/8-\delta_B$, $3/8-\delta_B$	$3/8-\delta_B$, $1/8+\delta_B$, $3/8-\delta_B$	$3/8-\delta_B$, $3/8-\delta_B$, $1/8+\delta_B$
Coordinates of B atoms in the structure of $F\bar{4}3m$ pyrochlore (in the basis of the structure $F\bar{4}3m$ pyrochlore)	*x*, *x*, *x*	*x*, -*x*, -*x*	-*x*, *x*, -*x*	-*x*, -*x*, *x*

Atoms B occupy Wyckoff positions 16*e* (*x*, *x* ,*x*), where $x = 1/8+\delta_B = 0.125+\delta_B$ in the structure of ordered $F\bar{4}3m$ pyrochlore

Table S3. Atom X coordinates at position 48*f* of the pyrochlore structure

Atom number	1	2	3	4	5	6	7	8	9	10	11	12
Coordinates of X atoms in the $Fd\bar{3}m$ structure of pyrochlore	x, 1/2, 1/2	1/2, *x*, 1/2	1/2, 1/2, *x*	1/4 +*x*, 1/4, 1/4	1/4, 1/4 +*x*, 1/4	1/4, 1/4, 1/4 +*x*	1-*x*, 1/2, 1/2	1/2, 1-*x*, 1/2	1/2, 1/2, 1-*x*	1/4-*x*, 1/4, 1/4	1/4, 1/4-*x*, 1/4	1/4, 1/4, 1/4-*x*
Scalar basic functions	1	1	1	-1	-1	-1	1	1	1	-1	-1	-1
Vector basis functions (displacements of atoms X)	100	010	001	-100	0-10	00-1	-100	0-10	00-1	100	010	001
Coordinates of X atoms in the structure of $F\bar{4}3m$ pyrochlore (in the basis of the structure $Fd\bar{3}m$ of pyrochlore)	$x+\delta_X$, 1/2, 1/2	1/2, $x+\delta_X$, 1/2	1/2, 1/2, $x+\delta_X$	1/4 +*x*-δ_X, 1/4, 1/4	1/4, 1/4 +*x*-δ_X, 1/4	1/4, 1/4, 1/4 +*x*-δ_X	1-*x*-δ_X, 1/2, 1/2	1/2, 1-*x*-δ_X, 1/2	1/2, 1/2, 1-*x*-δ_X	1/4-*x*+δ_X, 1/4, 1/4	1/4, 1/4-*x*+δ_X, 1/4	1/4, 1/4, 1/4-*x*+δ_X
Coordinates of X atoms in the structure of $F\bar{4}3m$ pyrochlore (in the basis of the structure $F\bar{4}3m$ pyrochlore)	x_1 0, 0	0, x_1 0	0, 0, x_1	x_2 1/4, 1/4	1/4, x_2, 1/4	1/4, 1/4, x_2	-x_1 0, 0	0, -x_1 0	0, 0, -x_1	x_2 1/4, 1/4	1/4, x_2, 1/4	1/4, 1/4, x_2
Wyckoff position	24*f*	24*f*	24*f*	24*g*	24*g*	24*g*	24*f*	24*f*	24*f*	24*g*	24*g*	24*g*

Atoms X occupy Wyckoff positions 24*f* (x_1=*x*+δ_X+1/2) and 24*g* (x_2=1/4 +*x*-δ_X) where *x*- free parameter of Wyckoff position 48*f* in the initial $Fd\bar{3}m$-pyrochlore, δ_X-magnitude of displacement

Table S4. Atom Y coordinates at position 8*b* of the pyrochlore structure

Atom number	1	2
Coordinates of Y atoms in the $Fd\bar{3}m$ structure of pyrochlore	1/2, 1/2, 1/2	3/4, 3/4, 3/4
Scalar basic functions	1	-1
Coordinates of Y atoms in the structure of $F\bar{4}3m$ pyrochlore (in the basis of the structure $Fd\bar{3}m$ of pyrochlore)	1/2, 1/2, 1/2	3/4, 3/4, 3/4
Coordinates of Y atoms in the structure of $F\bar{4}3m$ pyrochlore (in the basis of the structure $F\bar{4}3m$ pyrochlore)	1/2, 1/2, 1/2	3/4, 3/4, 3/4
Wyckoff position	4*b*	4*d*

Table S5. The role of order parameters in the $Fd\bar{3}m \rightarrow F\bar{4}3m$ phase transitions in $Ce_2Zr_2O_{7+\sigma}$[1] and NH_4NbWO_6.[2,3] The amplitudes normalized with respect to the primitive unit cell of the parent phase.

Irrep	Atom Wyckoff position	Amplitudes of distortions (Å)	
		$Ce_2Zr_2O_{7+\sigma}$	NH_4NbWO_6
$\mathbf{k_{11}}\tau_4(\Gamma_1^+)$	48*f*	0.45373	0.26247
	All	0.45373	0.26247
$\mathbf{k_{11}}\tau_4(\Gamma_2^-)$	16*d*	0.12223	-*
	16*c*	0.14445	0.17222
	48*f*	0.46114	0.26966
	All	0.49845	0.31996
Total	All	0.67404	0.41384*

*- displacement of ion NH_4^+ was not taken into account

References

1. S. N. Achary, S. K. Sali, N. K. Kulkarni, P. S. R. Krishna, A. B. Shinde and A. K. Tyagi, *Chem. Mater*. 2009, **21**, 5848.

2. P. W. Barnes, P. M. Woodward, Y. Lee, T. Vogt and J. A. Hriljac, *J. Am. Chem. Soc*., 2003, **125**, 4572.

3. C. A. Perottoni, J. Haines and J. A. H. da Jornada, *J. Solid State Chem*., 1998, **141**, 537.