Electronic Supplementary Information for

Influence of Phase transition from Order to Disorder and Philip's Ionicity on Thermal Expansion Coefficient of Pyrochlore Type Compositions with Multivalent Environment

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1. Table 1: Factor Group analysis for Pyrochlore structure

Modes	Distribution of degrees of freedom			Number of normal modes		
	A and B cations D_{3d} 16c, 16d	X anion C_2 48f	O anion T_d 8a	Acoustic modes	Lattice modes	Selection rules
A1g	0	1	0	0	1	Raman
A2g	0	0	0	0	0	Inactive
Eg	0	1	0	0	1	Raman
T1g	0	2	0	0	2	Inactive
T2g	0	3	1	0	4	Raman
A1u	0	0	0	0	0	Inactive
A2u	2	1	0	0	3	Inactive
Eu	2	1	0	0	3	Inactive
T1u	4	3	1	1	7	Infrared
T2u	2	2	0	0	4	Inactive

The factor group analysis of pyrochlore structured compositions is shown in Table 1.

2. Fractional Ionicity Calculation: Equations

$$E_h^{\mu} = \frac{39.74}{(d^{\mu})^{2.48}}$$

For any binary crystals A_mB_n type compounds, the hetero polar C^{μ} parts can be calculated as follows:

$$C^{\mu} = 14.4b^{\mu}exp\left(-k_s^{\mu}r_0^{\mu}\right)\left[Z_A^{\mu} - \frac{n}{m}Z_B^{\mu}\right]\frac{1}{r_0^{\mu}}$$

Where n>m

$$C^{\mu} = 14.4b^{\mu}exp\left(-k_s^{\mu}r_0^{\mu}\right)\left[\frac{m}{n}Z_A^{\mu} - Z_B^{\mu}\right]\frac{1}{r_0^{\mu}}$$

Where m>n

$$b^{\mu} = b(N_C^{\mu})^2$$

Where

$$k_s^{\mu} = \left(\frac{4k_f^{\mu}}{\prod a_B}\right)^{\frac{1}{2}}$$

$$k_f^{\mu} = \left(3\prod{}^2 N_e^{\mu}\right)^{\frac{1}{3}}$$

$$r_0^{\mu} = \frac{d_{\mu}}{2}$$

a_B is the Bohr radius (in Å) and d^{μ} is the bond distance (in Å). The units of E_h^{μ} and C^{μ} are in electron volts. The hetero polar energy gives a measure for the difference of screened coulomb potentials of the two atoms composing the bond or interaction of the point charges while the homo polar energy is a measure of the interaction of dipole and other multiple moments.[1] $exp(-k_s^{\mu}r_0^{\mu})$ is the Thomas-Fermi screening factor. k_f^{μ} is the Fermi wave vector. b^{μ} is the correction factor proportional to the square of the average coordination number N_c^{μ}.

$$b^{\mu} = \beta\left(N_c^{\mu}\right)^2$$

$$N_c^{\mu} = \frac{m}{m+n} N_{CA}^{\mu} + \frac{n}{m+n} N_{CB}^{\mu}$$

β is 0.089.[2] N_{CA}^{μ} is the coordination number of the μ type of bond for cation A, and N_{CB}^{μ} is the coordination number of the bond for anion B. N_e^{μ} is the number of valence electrons of the μ type of bond per cubic centimetre.

$$N_e^{\mu} = \frac{n_e^{\mu}}{\vartheta_b^{\mu}}$$

$$n_e^{\mu} = \frac{Z_A^{\mu}}{N_{CA}^{\mu}} + \frac{Z_B^{\mu}}{N_{CB}^{\mu}}$$

Where $n_e^{\mu}$is the number of effective valence electrons per μ bond and ϑ_b^{μ} is the bond volume.

$$\vartheta_b^{\mu} = \frac{\left(d^{\mu}\right)^3}{\sum_v \left(d^v\right)^3 N_b^v}$$

N_b^v is the number of bonds per cubic centimetre, which is obtained from the crystal structure

1 Z. J. Wu and S. Y. Zhang, *J. Phys. Chem. A*, 1999, **103**, 4270–4274.

2 B. F. Levine, *J. Chem. Phys.*, 1973, **59**, 1463.