Supporting information

Phase stability determination of negative thermal expansion silicates by theory and experiment

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Table S1. Lattice parameters [Å] of HT and LT phase calculated using DFT calculations and available experimental data.

Sample		DFT			Experiment		
		A	*b*	*c*	*a*	*b*	*c*
BaZn[a]	LT	7.181	12.691	13.680	7.277	12.799	13.687
	HT	7.802	12.956	6.614	7.610[b]	13.004[b]	6.719[b]
BaMg50	LT	7.146	12.603	13.767			
	HT	7.760	12.981	6.641			
Sr50Zn[c]	HT	7.717	12.938	6.528	7.692[d]	12.958[d]	6.562[d]
Sr50Mg50[c]	LT	7.100	12.601	13.518			
	HT	7.709	12.951	6.541	7.659[e]	12.956[e]	6.563[e]
Sr25Mg75	LT	7.130	12.579	13.634			
	HT	7.719	12.968	6.611			

[a] Experimental values taken from Ref. 5

[b] Measured at 550 K

[c] Experimental values taken from Ref. 6

[d] Only HT phase obtained from glass crystallization

[e] Experimental values for $Ba_{0.5}Sr_{0.5}Zn_{1.3}Mg_{0.7}Si_2O_7$ ($x = 0.5$, $y = 0.35$)

Table S2. Summary of **k**-point grids used for DFT simulations (using VASP with a **k**-point density of 13 1/Å^{-1}) and calculation of thermodynamic quantities from phonon frequencies (using phonopy with a **k**-point density of 140 1/Å^{-1}) for the original unit cells of the low (LT) and high temperature (HT) phase and their supercells (supercell size in brackets).

Unit cell	DFT simulations	Phonon properties
LT (1×1×1)	2×1×1	-
HT (1×1×1)	2×1×2	-
LT (2×1×1)	1×1×1	11×11×11
HT (2×1×2)	1×1×1	11×11×11

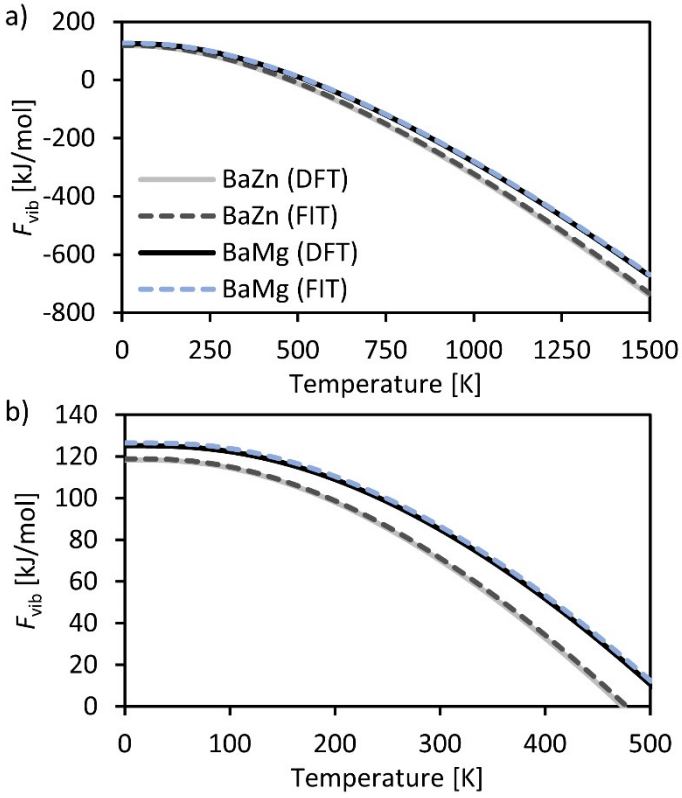

Figure S1. (a) Harmonic vibrational free energies F_{vib} of the high temperature phases of BaZn and BaMg calculated from phonon calculations (DFT) and the fitted model functions (FIT, eqs 1-8). (b) Low temperature range of (a).

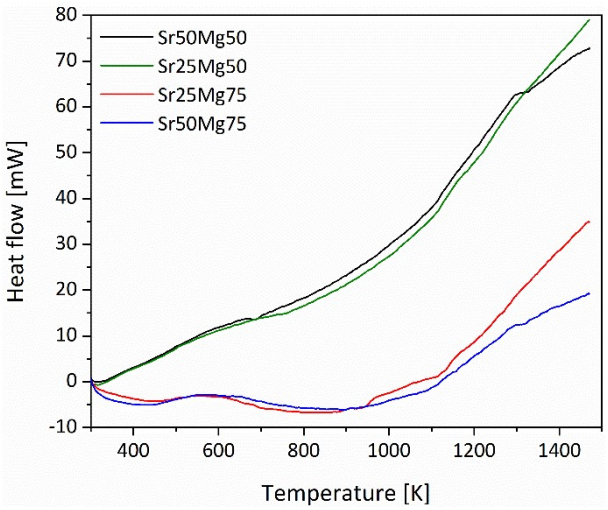

Figure S2. DSC profiles of the synthesized materials.

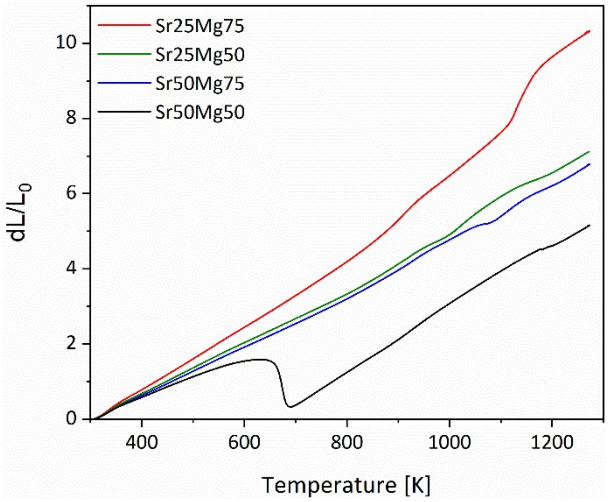

Figure S3. Results from dilatometry.

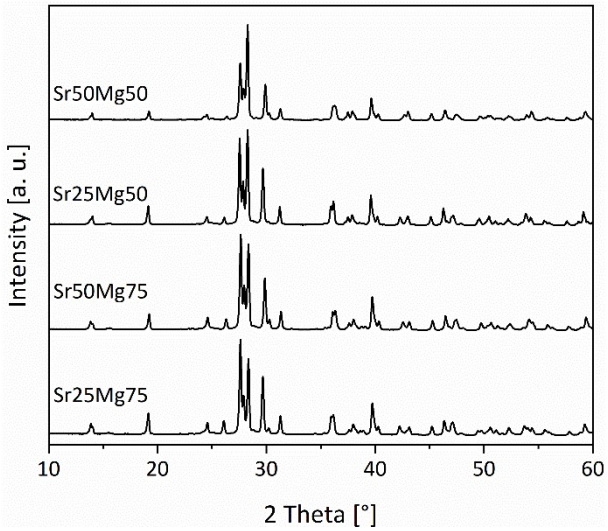

Figure S4. XRD patterns of the obtained compositions.