Supporting Information

Theoretical Prediction of Negative Thermal Expansion in Cubic VF$_3$

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Figure S1. The 3×3×3 supercell structure of (a) VF₃ and (b) ScF₃.

Figure S2. (a) Calculated band structure (b) density of states of cubic VF₃. (c) d-orbitals of V atom. Red dashed line indicates Fermi level.

Figure S3. Calculated thermodynamic properties of VF₃ versus temperature: (a) bulk modulus ($B$);
(b) heat capacities ($C_p$).

Figure S4. (a) Phonon dispersion (b) NTE and unit volume versus temperature (c) Phonon mode Grüneisen parameter (d) Grüneisen parameter along high symmetry direction of cubic ScF$_3$

Figure S5. (a) Electron localization function (ELF) (isosurface value: 0.6 born$^{-3}$) of ScF$_3$, Red, brown atoms denote V and F atoms, respectively. (b) The calculated COHP of ScF$_3$.

Figure S6. Calculated mode Grüneisen parameters of cubic supercell V$_{27}$F$_{81}$ with 0 e and 1 e, respectively. (1e/f.u.: adding one electron into the supercell V$_{27}$F$_{81}$)
Table S1. Elastic properties of cubic VF₃.

<table>
<thead>
<tr>
<th></th>
<th>C₁₁ (GPa)</th>
<th>C₁₂ (GPa)</th>
<th>C₄₄ (GPa)</th>
<th>B (GPa)</th>
<th>G (GPa)</th>
<th>E (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>VF₃</td>
<td>299.26</td>
<td>35.29</td>
<td>25.73</td>
<td>123.28</td>
<td>53.09</td>
<td>139.27</td>
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Table S2. Calculated Grüneisen parameters(γᵢ) of cubic VF₃ at the M (0.5, 0.5, 0) and R (0.5, 0.5, 0.5) points, and compared with isostructural ScF₃ and ReO₃.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>M (0.5, 0.5, 0) Frequency (cm⁻¹)</th>
<th>γᵢ (°K⁻¹)</th>
<th>R (0.5, 0.5, 0.5) Frequency (cm⁻¹)</th>
<th>γᵢ (°K⁻¹)</th>
<th>Maximum NTE (×10⁶ K⁻¹)</th>
<th>References</th>
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<tbody>
<tr>
<td>VF₃</td>
<td>72.48</td>
<td>-12.53</td>
<td>74.47</td>
<td>-11.82</td>
<td>-6.41 (80 K)</td>
<td>This work</td>
</tr>
<tr>
<td>ScF₃</td>
<td>34.92</td>
<td>-57.72</td>
<td>34.65</td>
<td>-98.81</td>
<td>-32.72 (160 K)</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>34.85</td>
<td>-57.72</td>
<td>34.65</td>
<td>-98.81</td>
<td>-32.72 (160 K)</td>
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