**Supplemental Table S1. Bond-valence calculations (Brown & Altermatt, 1985) for dargaite**

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | O1 | O2 | O3 | O4 | O5 | O6 | O7 | O8 | Sum |
| Ba1 | 0.174 6→ |  | 0.0596→ |  |  |  |  |  | 1.40 |
| Ca1 | 0.1662→↓ |  | 0.3402→↓ | 0.2293↓ | 0.3423↓ |  | 0.3183↓ |  | 1.901 |
| Ca2 |  | 0.3712→↓  0.192 | 0.126 |  |  | 0.3843↓ | 0.2573↓ | 0.3906↓ | 2.091 |
| S1 | 1.4563→ |  |  | 1.468 |  |  |  |  | 5.836 |
| Si1 |  | 0.9873→ |  |  | 0.912 |  |  |  | 3.873 |
| Si2 |  |  | 1.0363→ |  |  | 0.984 |  |  | 4.092 |
|  | 1.962 | 1.921 | 1.901 | 2.155 | 1.938 | 2.136 | 1.725 | 2.340 |  |

Ba1 = 0.7Ba+0.3K; O7 = 0.77O+0.23F

**Supplemental Table S2. Bond-valence calculations (Brown & Altermatt, 1985) for synthetic KCa12(SiO4)4(SO4)2O2F (Fayos et al., 1985)**

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | O1 | O2 | O3 | O4 | O5 | O6 | O7 | O8 | Sum |
| K1 | 0.120 6→ |  | 0.0346→ |  |  |  |  |  | 0.924 |
| Ca1 | 0.1802→↓ |  | 0.3392→↓ | 0.2263↓ | 0.3493↓ |  | 0.2713↓ |  | 1.884 |
| Ca2 |  | 0.3542→↓  0.188 | 0.170 |  |  | 0.4193↓ | 0.2313↓ | 0.3746↓ | 2.090 |
| S1 | 1.5293→ |  |  | 1.444 |  |  |  |  | 6.031 |
| Si1 |  | 1.0253→ |  |  | 0.935 |  |  |  | 4.010 |
| Si2 |  |  | 0.9873→ |  |  | 0.925 |  |  | 3.886 |
|  | 2.009 | 1.921 | 1.869 | 2.122 | 1.982 | 2.182 | 1.506 | 2.244 |  |

O7 = 0.5O+0.5F

**Supplemental Table S3. Bond-valence calculations (Brown & Altermatt, 1985) for nabimusaite (Galuskin et al., 2015a)**

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | O1 | O2 | O3 | O4 | O5 | O6 | O7 | O8 | Sum |
| K1 | 0.141 6→ |  | 0.0436→ |  |  |  |  |  | 1.104 |
| Ca1 | 0.1672→↓ |  | 0.3472→↓ | 0.2283↓ | 0.3503↓ |  | 0.2783↓ |  | 1.884 |
| Ca2 |  | 0.3662→↓  0.195 | 0.148 |  |  | 0.4103↓ | 0.2393↓ | 0.3766↓ | 2.100 |
| S1 | 1.5083→ |  |  | 1.460 |  |  |  |  | 5.984 |
| Si1 |  | 0.9843→ |  |  | 0.869 |  |  |  | 3.821 |
| Si2 |  |  | 1.0003→ |  |  | 0.942 |  |  | 3.942 |
|  | 1.983 | 1.911 | 1.885 | 2.144 | 1.919 | 2.172 | 1.551 | 2.256 |  |

K1 = 0.73K+0.27Ba; O7 = 0.5O+0.5F