**Table 1**. The coordinate and charge of each atom in unit cell of NaFe3Al6(Si6O18)(BO3)3(OH)4 after geometry optimization

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Atom | *x* | *y* | *z* | charge | Atom | *x* | *y* | *z* | charge |
| H1 | 6.3745 | 2.4966 | 2.4966 | 0.42 | O21 | 3.8148 | 7.8157 | 3.8147 | -0.9 |
| H2 | 2.4965 | 6.3744 | 2.4964 | 0.42 | O22 | -0.0547 | 2.8379 | -0.0548 | -1.14 |
| H3 | 2.4962 | 2.4962 | 6.3743 | 0.42 | O23 | 3.8145 | 3.8145 | 7.8156 | -0.9 |
| H4 | 8.8609 | 8.8615 | 8.8625 | 0.32 | O24 | -0.0550 | -0.0550 | 2.8377 | -1.14 |
| B1 | 5.7261 | 5.7261 | 2.3909 | 0.89 | O25 | 5.6319 | 5.6319 | 3.7501 | -0.71 |
| B2 | 2.3905 | 5.7258 | 5.7258 | 0.89 | O26 | 1.5274 | 1.5274 | -1.1712 | -1.15 |
| B3 | 5.7260 | 2.3906 | 5.7259 | 0.89 | O27 | 3.7495 | 5.6313 | 5.6313 | -0.71 |
| O1 | 9.7114 | 7.5821 | 5.7648 | -1.04 | O28 | -1.1711 | 1.5271 | 1.5270 | -1.15 |
| O2 | 3.6379 | 0.8503 | -2.1016 | -1.13 | O29 | 5.6315 | 3.7497 | 5.6316 | -0.71 |
| O3 | 6.5232 | 5.0154 | 1.6816 | -0.93 | O30 | 1.5272 | -1.1712 | 1.5272 | -1.15 |
| O4 | 5.7647 | 9.7113 | 7.5820 | -1.04 | O31 | 7.5002 | 7.5003 | 7.5004 | -0.65 |
| O5 | -0.21014 | 3.6379 | 0.8503 | -1.13 | Na1 | 2.7824 | 2.7823 | 2.7821 | 1.46 |
| O6 | 1.6813 | 6.5231 | 5.0153 | -0.93 | Al1 | 9.0777 | 5.7137 | 3.4769 | 1.75 |
| O7 | 7.5818 | 5.7646 | 9.7112 | -1.04 | Al2 | 3.4768 | 9.0778 | 5.7136 | 1.75 |
| O8 | 0. 8503 | -2.1016 | 3.6378 | -1.13 | Al3 | 5.7136 | 3.4768 | 9.0777 | 1.75 |
| O9 | 5.0152 | 1.6813 | 6.5229 | -0.93 | Al4 | 5.7137 | 9.0777 | 3.4768 | 1.75 |
| O10 | 7.5820 | 9.7113 | 5.7648 | -1.04 | Al5 | 9.0778 | 3.4769 | 5.7136 | 1.75 |
| O11 | 0.8503 | 3.6378 | -2.1016 | -1.13 | Al6 | 3.4768 | 5.7136 | 9.0777 | 1.75 |
| O12 | 5.0153 | 6.5231 | 1.6815 | -0.93 | Si1 | 1.8845 | -0.0750 | -1.9622 | 2.11 |
| O13 | 9.7114 | 5.7648 | 7.5821 | -1.04 | Si2 | -1.9622 | 1.8848 | -0.0752 | 2.11 |
| O14 | 3.6379 | -2.1015 | 0.8503 | -1.13 | Si3 | -0.0752 | -1.9624 | 1.8846 | 2.11 |
| O15 | 6.5232 | 1.6815 | 5.0154 | -0.93 | Si4 | -0.0751 | 1.8848 | -1.9623 | 2.11 |
| O16 | 5.7646 | 7.5819 | 9.7112 | -1.04 | Si5 | 1.8849 | -1.9621 | -0.0751 | 2.11 |
| O17 | -2.1015 | 0.8503 | 3.6378 | -1.13 | Si6 | -1.9623 | -0.0753 | 1.8846 | 2.11 |
| O18 | 1.6812 | 5.0152 | 6.5229 | -0.93 | Fe1 | 7.6413 | 5.6927 | 5.6927 | 0.7 |
| O19 | 7.8158 | 3.8149 | 3.8149 | -0.9 | Fe2 | 5.6924 | 7.6410 | 5.6925 | 0.7 |
| O20 | 2.8380 | -0.0546 | -0.0547 | -1.14 | Fe3 | 5.6921 | 5.6921 | 7.6407 | 0.7 |

**Table 2**. Comparison of R-O bond lengths of dravite NaMg3Al6(Si6O18)(BO3)3(OH)3(OH) and oxy-dravite Na(MgAl2)(Al5Mg)(Si6O18)(BO3)3(OH)3O

|  |  |  |  |
| --- | --- | --- | --- |
| Polyhedra | Na(MgAl2)(Al5Mg)(Si6O18)(BO3)3(OH)3O | Polyhedra | NaMg3Al6(Si6O18)(BO3)3(OH)3(OH) |
| Cation | Anion | Bond length | Cation | Anion | Bond length | Cation | Anion | Bond length | Cation | Anion | Bond length |
| *Y* | Al001 | O031 | 17.7901 | Al007 | O031 | 17.7079 | Mg002 | O031 | 20.6218 | *Y* | Mg001 | O029 | 20.4790 |
| O001 | 18.1199 | O027 | 18.8827 | O007 | 20.6393 | Mg001 | O025 | 20.4797 |
| O029 | 18.8252 | O004 | 18.9153 | O027 | 20.8305 | Mg001 | O031 | 20.7195 |
| O013 | 19.3221 | O025 | 19.0181 | O016 | 20.8886 | Mg001 | O013 | 20.7850 |
| O019 | 20.6658 | O010 | 19.6228 | O029 | 20.8960 | Mg001 | O001 | 20.7859 |
| O025 | 20.7704 | O021 | 21.5956 | O023 | 21.9885 | Mg001 | O019 | 21.6276 |
| Mean |  | 19.2489 |  |  | 19.2904 |  |  | 20.9775 | Mean |  | 20.8128 |
| *Z* | Mg001 | O001 | 20.2518 | Al002 | O008 | 17.7499 | Al003 | O003 | 17.9830 | *Z* | Al001 | O001 | 17.8162 |
| O005 | 20.2856 | O006 | 17.9665 | O007 | 18.1048 | O005 | 18.1667 |
| O006 | 20.2962 | O009 | 18.8930 | O005 | 18.3355 | O006 | 18.3043 |
| O003 | 20.7953 | O002 | 18.9377 | O002 | 18.6172 | O003 | 19.2014 |
| O008 | 21.2915 | O004 | 18.9732 | O009 | 19.3069 | O008 | 19.4798 |
| O019 | 21.4433 | O021 | 20.5784 | O023 | 20.1093 | O019 | 19.6954 |
| Mean |  | 20.7273 |  |  | 18.8498 |  |  | 18.7428 | Mean |  | 18.7773 |
| Al004 | O014 | 18.4156 | Al005 | O017 | 18.3568 | Al006 | O016 | 17.8409 |  |  |  |  |
| O010 | 18.4569 | O013 | 18.7337 |  | O011 | 18.5663 |  |  |  |  |
| O015 | 18.4751 | O019 | 18.7646 |  | O012 | 18.6587 |  |  |  |  |
| O012 | 18.6478 | O015 | 18.9263 |  | O018 | 19.1494 |  |  |  |  |
| O021 | 19.3426 | O018 | 19.1669 |  | O023 | 19.2540 |  |  |  |  |
| O017 | 19.5375 | O011 | 19.2429 |  | O014 | 19.9959 |  |  |  |  |
| Mean |  | 18.8126 |  | Mean | 18.8652 |  |  | 18.9109 |  |  |  |  |

**Table 3**. The tourmaline spedies to simulate the substitution and order-disorder reactions scheme reported by Menken (2014)

|  |  |
| --- | --- |
| Disorder and exchange scheme | Tourmaline species to be compared |
| Before virtual heat treatment | After virtual heat treatment |
| YFe2+ +ZAl + OH ↔ZFe3+ + YAl + O + H↑ | NaFe3Al6(Si6O18)(BO3)3(OH)4 | Na(AlFe2)(Al5Fe)(Si6O18)(BO3)3(OH)3O |
| YMg + ZAl↔ZMg + YAl | NaMg3Al6(Si6O18)(BO3)3(OH)3F | Na(AlMg2)(Al5Mg)(Si6O18)(BO3)3(OH)3F |
| NaMg3Al6(Si6O18)(BO3)3(OH)4 | Na(AlMg2)(Al5Mg)(Si6O18)(BO3)3(OH)4 |

**Table 4**. The simulation results of average bond length before and after disordering at *X*, *Y* site

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Tourmaline species | Disordering | Polyhedron | Average bond length | Variation |
| Before disordering | After disordering |
| NaFe3Al6(Si6O18)(BO3)3(OH)4 | *Y*Fe↔*Z*Al*W*OH↔*W*O | *Y* | 20.1277 | 19.7966 | -0.3310 |
| *Z* | 18.8282 | 19.0483 | 0.2201 |
| NaMg3Al6(Si6O18)(BO3)3(OH)3F | *Y*Mg↔*Z*Al | *Y* | 20.7530 | 20.1471 | -0.6056 |
| *Z* | 18.7940 | 19.0844 | 0.2903 |
| NaMg3Al6(Si6O18)(BO3)3(OH)4 | *Y*Mg↔*Z*Al | *Y* | 20.8128 | 20.2098 | -0.6030 |
| *Z* | 18.7773 | 19.0656 | 0.2883 |

**Table 5**. Intrinsic dipole moments of several tourmaline species

|  |  |
| --- | --- |
| Chemical compositionin unit cell | Intrinsic dipole moment(*P*),×10-29∙C∙m |
| *Pu* | *Pv* | *Pw* | *P*C (projective value along c axis) |
| NaFe3Al6(Si6O18)(BO3)3(OH)3F | -20.6505 | -20.6505 | -20.6505 | 20.6505 |
| NaMg3Al6(Si6O18)(BO3)3(OH)3F | -19.4277 | -19.4277 | -19.4277 | 19.4277 |
| NaFe3Al6(Si6O18)(BO3)3(OH)4 | -18.3495 | -18.3495 | -18.3480 | 18.3490 |
| NaMg3Al6(Si6O18)(BO3)3(OH)4 | -18.8247 | -18.8247 | -18.8277 | 18.8257 |

*Pu,Pv* and*Pw are u,v* and *w*components of the intrinsic dipole moment.

**Table 6**. Intrinsic dipole moments of different tourmalines speices

|  |  |  |  |
| --- | --- | --- | --- |
| № | Mineral name | Chemical composition in unit cell | Electric dipole moment |
| Fractional components | Size |
| *x* | *y* | *z* |
| 1 | Heated fluor -schorl | NaFe3Al6(Si6O18)(BO3)3(OH)3F | -20.6505 | -20.6505 | -20.6505 | 20.6505 |
| 2 | Schorl | NaFe3Al6(Si6O18)(BO3)3(OH)4 | -18.3495 | -18.3495 | -18.348 | 18.349 |
| 3 | Heated oxy-schorl | Na(AlFe2 )(Al5Fe)(Si6O18)(BO3)3(OH)3O | -19.647 | -25.432 | -22.3438 | 22.4743 |
| 4 | Fluoro-dravite | NaMg3Al6(Si6O18)(BO3)3(OH)3F | -19.4277 | -19.4277 | -19.4277 | 19.4277 |
| 5 | dravite | NaMg3Al6(Si6O18)(BO3)3(OH)4 | -18.8247 | -18.8247 | -18.8277 | 18.8257 |
| 6 | Heated fluor-dravite | Na(AlMg2)(Al5Mg)(Si6O18)(BO3)3(OH)3F | -17.8455 | -19.4064 | -18.2612 | 18.5044 |
| 7 | Heated dravite | Na(AlMg2)(Al5Mg)(Si6O18)(BO3)3(OH)4 | -17.1146 | -18.2978 | -17.3704 | 17.5942 |
| 8 | Heated oxy-dravite | Na(MgAl2 )(Al5Mg)(Si6O18)(BO3)3(OH)3O | -19.8312 | -19.1231 | -19.5525 | 19.5023 |
| 9 | Mg-rich fluor-schorl | Na(Fe2Mg)Al6(Si6O18)(BO3)3(OH)3F | -20.2743 | -20.014 | -20.014 | 20.1007 |
| 10 | Fe-rich fluor-dravite | Na(FeMg2 )Al6(Si6O18)(BO3)3(OH)3F | -19.3835 | -19.3835 | -18.9861 | 19.251 |
| 11 | Mg-rich schorl | Na(Fe2Mg)Al6(Si6O18)(BO3)3(OH)4 | -18.8125 | -18.8094 | -19.0972 | 18.9064 |
| 12 | Fe-rich dravite | Na(FeMg2)Al6(Si6O18)(BO3)3(OH)4 | -18.2658 | -18.2658 | -18.1851 | 18.2389 |
| 13 | Fe-rich fluor-elbaite | Na(FeAlLi)Al6(Si6O18)(BO3)3(OH)3F | -18.7028 | -19.5282 | -17.4816 | 18.5709 |
| 14 | Fe-rich elbaite | Na(FeAlLi)Al6(Si6O18)(BO3)3(OH)4 | -18.7531 | -18.5917 | -16.9471 | 18.0973 |
| 15 | Mg-rich fluor-elbaite | Na(MgAlLi)Al6(Si6O18)(BO3)3(OH)3F | -18.8612 | -18.8551 | -16.8968 | 18.2044 |
| 16 | Mg-rich elbaite | Na(MgAlLi)Al6(Si6O18)(BO3)3(OH)4 | -18.0983 | -18.1424 | -15.9755 | 17.4054 |
| 17 | Fluor-buergerite | NaFe3Al6(Si6O18)(BO3)3O3F | 19.38656 | 19.38656 | 19.38656 | 19.3866 |
| 18 | Buergerite | NaFe3Al6(Si6O18)(BO3)3O3OH | 18.10133 | 18.10133 | 18.10133 | 18.1013 |
| 19 | Feruvite | CaFe3(Al5Mg)(Si6O18)(BO3)3(OH)4 | -17.9536 | -19.012 | -19.4627 | 18.8094 |
| 20 | Fluor-uvite | CaMg3(Al5Mg)(Si6O18)(BO3)3(OH)3F | -19.3607 | -20.4068 | -20.9002 | 20.2226 |
| 21 | Fluor-liddicoatite | Ca(Li2Al)Al6(Si6O18)(BO3)3(OH)3F | -21.6509 | -21.6509 | -19.0851 | 20.7956 |
| 22 | Lucchesiite | CaFe3Al6(Si6O18)(BO3)3(OH)3O | 22.72451 | 22.72451 | 22.72451 | 22.7245 |
| 23 | Mg-analog of lucchesiite | CaMg3Al6(Si6O18)(BO3)3(OH)3O | 23.48133 | 23.48133 | 23.48133 | 23.4813 |
| 24 | Magnesio-foitite | (Mg2Al)Al6(Si6O18)(BO3)3(OH)4 | -14.8289 | -14.8304 | -13.2208 | 14.2934 |
| 25 | Foitite | (Fe2Al)Al6(Si6O18)(BO3)3(OH)4 | -15.4776 | -15.4791 | -13.8497 | 14.9355 |
| 26 | Rossmanite | (LiAl2)Al6(Si6O18)(BO3)3(OH)4 | -18.3511 | -14.9903 | -14.9903 | 16.1105 |

**Appendix 1**

|  |  |  |  |
| --- | --- | --- | --- |
| Polyhedra | Na(AlFe2)(Al5Fe)(Si6O18)(BO3)3(OH)3O | Polyhedra | NaFe3Al6(Si6O18)(BO3)3(OH)4 |
| Cation | Anion | Bond length | Cation | Anion | Bond length | Cation | Anion | Bond length | Cation | Anion | Bond length |
| *Y* | Al 001 | O 031 | 18.0252 | Fe 002 | O 031 | 19.2951 | Fe 003 | O 031 | 19.2481 | *Y* | Fe 001 | O 031 | 19.7626 |
| O 001 | 18.4435 | O 027 | 19.8240 | O 027 | 19.6174 | O 025 | 20.0638 |
| O 025 | 18.8552 | O 004 | 19.8787 | O 007 | 19.8932 | O 029 | 20.0647 |
| O 029 | 19.0325 | O 010 | 20.1487 | O 029 | 20.2006 | O 001 | 20.0688 |
| O 013 | 19.9497 | O 025 | 20.2355 | O 016 | 20.2289 | O 013 | 20.0688 |
| O 019 | 20.6004 | O 021 | 21.4621 | O 023 | 21.4002 | O 019 | 20.7372 |
| Mean |  | 19.1511 | Mean |  | 20.1407 | Mean |  | 20.0981 | Mean |  | 20.1277 |
| *Z* | Fe 001 | O 005 | 19.6952 | Al 002 | O 008 | 18.0188 | Al 003 | O 007 | 18.1256 | *Z* | Al 001 | O 001 | 17.8230 |
| O 001 | 19.6964 | O 004 | 18.1696 | O 003 | 18.1886 | O 005 | 18.1881 |
| O 006 | 19.7626 | O 006 | 18.2712 | O 005 | 18.4979 | O 006 | 18.5892 |
| O 003 | 19.8887 | O 002 | 19.1264 | O 002 | 18.7145 | O 003 | 19.1170 |
| O 008 | 20.3691 | O 009 | 19.1749 | O 009 | 18.9744 | O 019 | 19.5782 |
| O 019 | 20.4667 | O 021 | 20.0299 | O 023 | 20.1227 | O 008 | 19.6735 |
| Mean |  | 19.9798 | Mean |  | 18.7985 | Mean |  | 18.7706 | Mean |  | 18.8282 |
| Al 004 | O 010 | 18.0492 | Al 005 | O 017 | 18.4094 | Al 006 | O 016 | 18.0174 |  |  |  |  |
| O 014 | 18.4465 | O 013 | 18.4996 | O 011 | 18.3957 |  |  |  |  |
| O 015 | 18.8766 | O 018 | 18.7120 | O 012 | 18.8997 |  |  |  |  |
| O 012 | 18.9530 | O 015 | 18.9011 | O 018 | 19.0678 |  |  |  |  |
| O 021 | 19.1758 | O 011 | 19.5386 | O 023 | 19.3910 |  |  |  |  |
| O 017 | 19.8055 | O 019 | 19.5996 | O 014 | 19.7072 |  |  |  |  |
| Mean |  | 18.8844 | Mean |  | 18.9434 | Mean |  | 18.9131 |  |  |  |  |

 **Appendix 2**

|  |  |  |  |
| --- | --- | --- | --- |
| Polyhedra | Na(AlMg2)(Al5Mg)(Si6O18)(BO3)3(OH)3F | Polyhedra | NaMg3Al6(Si6O18)(BO3)3(OH)3F |
| Cation | Anion | Bondlength | Cation | Anion | Bondlength | Cation | Anion | Bondlength | Cation | Anion | Bondlength |
| *Y* | Al001 | O001 | 18.1124 | Mg002 | O004 | 20.3648 | Mg003 | O027 | 20.0374 | *Y* | Mg001 | O025 | 20.3510 |
| F001 | 18.2473 | O027 | 20.4301 | O007 | 20.2635 | O029 | 20.3510 |
| O029 | 18.5628 | O025 | 20.6768 | O029 | 20.9211 | F001 | 20.7602 |
| O019 | 18.8084 | O010 | 20.7691 | O016 | 20.9989 | O013 | 20.7776 |
| O025 | 18.9370 | O021 | 21.5497 | O023 | 21.1842 | O001 | 20.7776 |
| O013 | 19.3825 | F001 | 21.8536 | F001 | 21.5487 | O019 | 21.5005 |
| Mean |  | 18.6751 | Mean |  | 20.9407 | Mean |  | 20.8256 | Mean |  | 20.7530 |
| *Z* | Mg001 | O005 | 20.0199 | Al002 | O008 | 17.8133 | Al003 | O003 | 17.7160 | *Z* | Al001 | O001 | 17.8620 |
| O006 | 20.1111 | O004 | 17.9482 | O005 | 18.1373 | O005 | 18.2181 |
| O001 | 20.4133 | O006 | 18.2854 | O007 | 18.2296 | O006 | 18.3104 |
| O003 | 20.6625 | O002 | 19.0024 | O002 | 18.6788 | O003 | 19.2336 |
| O008 | 21.0376 | O009 | 19.2497 | O009 | 18.9204 | O008 | 19.4250 |
| O019 | 21.8167 | O021 | 20.0624 | O023 | 20.4302 | O019 | 19.7150 |
| Mean |  | 20.6769 | Mean |  | 18.7269 | Mean |  | 18.6854 | Mean |  | 18.7940 |
| Al004 | O010 | 17.9535 | Al005 | O017 | 18.2576 | Al006 | O016 | 17.8744 |  |  |  |  |
| O015 | 18.4257 | O018 | 18.4571 | O011 | 18.2891 |  |  |  |  |
| O014 | 18.4261 | O013 | 18.5878 | O012 | 18.8571 |  |  |  |  |
| O021 | 19.0678 | O015 | 18.8845 | O023 | 19.2718 |  |  |  |  |
| O012 | 19.1231 | O011 | 19.0891 | O018 | 19.3847 |  |  |  |  |
| O017 | 19.6191 | O019 | 19.2949 | O014 | 19.6386 |  |  |  |  |
| Mean |  | 18.7692 | Mean |  | 18.7618 | Mean |  | 18.8860 |  |  |  |  |

**Appendix 3**

|  |  |  |  |
| --- | --- | --- | --- |
| Polyhedra | Na(AlMg2)(Al5Mg)[Si6O18](BO3)3(OH)4 | Polyhedra | NaMg3Al6[Si6O18](BO3)3(OH)4 |
| Cation | Anion | Bondlength | Cation | Anion | Bondlength | Cation | Anion | Bondlength | Cation | Anion | Bondlength |
| *Y* | Al001 | O001 | 18.1518 | Mg002 | O004 | 20.4893 | Mg003 | O027 | 20.2000 | *Y* | Mg001 | O029 | 20.4790 |
| O029 | 18.4953 | O027 | 20.5065 | O007 | 20.2353 | O025 | 20.4797 |
| O031 | 18.6152 | O025 | 20.7735 | O016 | 20.7978 | O031 | 20.7195 |
| O019 | 18.9040 | O010 | 20.9974 | O029 | 21.1362 | O013 | 20.7850 |
| O025 | 18.9253 | O021 | 21.3958 | O031 | 21.2019 | O001 | 20.7859 |
| O013 | 19.7068 | O031 | 21.7519 | O023 | 21.4927 | O019 | 21.6276 |
| Mean |  | 18.7997 | Mean |  | 20.9857 |  |  | 20.8440 | Mean |  | 20.8128 |
| *Z* | Mg001 | O005 | 20.0136 | Al002 | O008 | 17.7383 | Al003 | O003 | 17.7356 | *Z* | Al001 | O001 | 17.8162 |
| O006 | 20.0813 | O004 | 17.8844 | O007 | 18.1227 | O005 | 18.1667 |
| O001 | 20.3314 | O006 | 18.2980 | O005 | 18.1819 | O006 | 18.3043 |
| O003 | 20.5683 | O002 | 18.8873 | O002 | 18.7081 | O003 | 19.2014 |
| O008 | 21.1252 | O009 | 19.4245 | O009 | 18.8350 | O008 | 19.4798 |
| O019 | 21.8195 | O021 | 20.1931 | O023 | 20.2056 | O019 | 19.6954 |
| Mean |  | 20.6566 | Mean |  | 18.7376 |  |  | 18.6315 | Mean |  | 18.7773 |
| Al004 | O010 | 17.8801 | Al005 | O017 | 18.2987 | Al006 | O016 | 17.8556 |  |  |  |  |
| O014 | 18.3713 | O018 | 18.3425 | O011 | 18.1940 |  |  |  |  |
| O015 | 18.4768 | O013 | 18.3890 | O012 | 18.7466 |  |  |  |  |
| O021 | 19.0165 | O015 | 18.7920 | O023 | 19.2634 |  |  |  |  |
| O012 | 19.2480 | O019 | 19.2816 | O018 | 19.5348 |  |  |  |  |
| O017 | 19.5071 | O011 | 19.3958 | O014 | 19.6143 |  |  |  |  |
| Mean |  | 18.7499 | Mean |  | 18.7499 | Mean |  | 18.8681 |  |  |  |  |