

Bond valences calculations and Bi-Pb occupancy at different cation sites

We made an estimation using the formula of Brown and Altermatt (1985) for the relation bond length-bond valence: $v = \exp[(R_0 - d)/b]$ where v is the valence, d the bond distance and R_0 and b the constants characteristic for a bonded pair of atoms. We assumed the following relation:

$$xv_{i1} + (1-x)v_{i2} = xv_{c1} + (1-x)v_{c2}$$

where x is the proportion of the first species, v_{i1} and v_{i2} are the expected valences of the first and the second species, and v_{c1} and v_{c2} are valences calculated for the site using the bond valence constants for the first and the second species, respectively. For x , we then get:

$$x = (v_{c2} - v_{i2}) / (v_{i1} - v_{c1} + v_{c2} - v_{i2})$$

To obtain the bond valence constants for the two species applicable at various pressures, we first assume the constant b equal to the suggested general value of 0.37 (Brown and Altermatt 1985). This leaves only R_0 as the bond valence parameter that has to be determined for each species. To evaluate the dependence of the R_0 on the pressure we used the data for Bi_2S_3 (Lundegaard et al. 2005) and PbS (Vaidya et al. 1973) at high-pressures. The R_0 values that give the expected valences were calculated by program Ivton (Balić-Žunić and Vicković 1996). For Bi_2S_3 we averaged the values obtained for two independent Bi sites that anyway give very small differences. For both sulfides, we obtained a linear dependence of R_0 on pressure:

$$\text{for Bi: } R_0 = 2.54227 - 0.00852P(\text{GPa})$$

$$\text{for Pb: } R_0 = 2.55789 - 0.01548P(\text{GPa})$$

The calculations give the following proportions of Bi for the low-pressure phase just before the phase transition (4.9 GPa): M1 0.63, M2 0.38, M3 -0.07 (the calculated values for lillianite at room pressure are: M1 0.51, M2 0.39, M3 -0.12.). For the high-pressure phase, at the first pressure after transition (6.3 GPa) the following proportions of Bi are obtained: for M1A 0.38, M1B 0.8, M2A 0.47, M2B 0.48 and M3 -0.04.

Our calculations for lillianite and β -Pb₃Bi₂S₆ are consistent in suggesting that Bi occupies in a small excess M1 sites and Pb M2 sites, whereas M3 is exclusively a Pb site. Although the summary result for occupancy of the two M1-type sites in β -Pb₃Bi₂S₆ fits well the result for lillianite, we cannot explain the quantitative difference between M1A, suggesting a small excess of Pb, and M1B, suggesting a large excess of Bi. If the content of Bi is the main reason for difference in coordination properties, we should assume that a diffusion of the Bi and Pb among the neighboring M1A and M1B sites occurs. This seems unlikely also considering the fact that on decompression the back-diffusion of the Pb and Bi atoms would be necessary to restore the lillianite structure. If, on the other hand, the ordering of this kind existed in lillianite before the phase transition, already the low-pressure lillianite would have the *Pbnm* symmetry and not the *Bbmm* symmetry, the latter being a consequence of a disorder in the M1 and M2 sites. One thing can though be concluded: the symmetry of the high-pressure phase developed from lillianite without the unlikely Bi-Pb diffusion excludes a model in which low-pressure lillianite consists of the homogeneous (010) slabs with the same ordering of atomic sites as in xilingolite, but with a disorder in the slabs' sequence. The disorder in lillianite is contained inside individual slabs; otherwise, the observed high-pressure structure would not be possible. It would be interesting to investigate the high-pressure behavior of xilingolite, but this mineral is very rare in the nature and the only crystal from which its structure could be determined was a very small twin. To the best of our knowledge, a compound with xilingolite structure was never synthesized. We conclude that the differences between the M coordinations in β -Pb₃Bi₂S₆ are primarily due to the structure type peculiarities and not to the occupancies/ordering of Pb and Bi.