Anti-Loewenstein behaviour in the melilite and sodalite structure types

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As Loewenstein [1] stated, "one of the most important features of the modern theory of silicates is the double rôle of aluminium, which can substitute for silicon in tetrahedra […]". Loewenstein based his rule, which is also known as aluminium-avoidance-Rule, on the observation that "in all known cases […] the maximum substitution is 50%". This led him to conclude that "no two aluminium ions can occupy the centers of tetrahedra linked by one oxygen". Ca2Al[AlSiO7], gehlenite, crystallizes in space group $P\bar{4}2_1m$ in the melilite structure type. It contains two topologically different tetrahedral positions, one of which is fully occupied by Al3+, whereas the second one contains Al3+ and Si4+. Normally the Al3+ molar fraction in the second tetrahedral position does not exceed xAl = 0.5, in accordance with Loewenstein's Rule. In this contribution we show that it is possible to substitute much more Al^{3+} for Si^{4+} than is allowed by Loewenstein's Rule. This happens via a coupled substitution of $(Re^{3+}+Al^{3+})$ for $(Ca^{2+}+Si^{4+})$. Compounds of the composition $Eu_xCa_{2-x}Al[Al_{1+x}Si_{1-x}O_7]$ and $La_xCa_{2-x}Al[Al_{1+x}Si_{1-x}O_7]$ with $0 < x < 1$ were synthesized at 1773 K, atmospheric pressure. Rietveld-refinements of powder diffraction patterns show that the single phased products crystallize in space group $P\bar{4}2_1m$, without changing the Wyckoff-positions of the ions in the melilite structure. Substitutions of a similar type were shown to be possible in the sodalite structure, starting from the mineral bicchulite, $Ca_8[Al_8Si_4O_{24}](OH)_8$. Note that the sodalite structure type contains only one topologically independent tetrahedral position. Solid solutions in the compositional range $Ca_8[Al_8Si_4O_{24}](OH)_8$ – $Eu_4Ca_4[Al_{12}O_{24}](OH)_8$ have been synthesized hydrothermally at 800-900 K, 0.1 GPa, starting from the melilite-type compounds. Up to date it has not been possible to synthesize the corresponding La homologues, presumably because of the significantly bigger ionic radius of La^{3+} compared with those of Ca^{2+} and Eu^{3+}. Up until now we have no answer to the question whether violations of Loewenstein's rule are restricted to particular structure types only, and if so, what makes the particularities of these structure types.

[1] Loewenstein, W. (1954): Amer. Min., **39**, 92-96

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