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The crystal structure of dissakisite-(La) and structural variations after annealing of radiation damage

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ABSTRACT

The crystal chemistry of the new mineral dissakisite-(La), the Mg-analogue of allanite-(La) with ideal formula $CaLaAl_2MgSi_3O_{12}(OH)$, was studied by single-crystal X-ray diffraction and Mössbauer spectroscopy. Diffraction data indicated that it has a partially metamict state with expanded cell parameters $a = 8.959$, $b = 5.7226$, and $c = 10.232$ Å, $\beta = 115.19°$, and $V = 474.7$ Å^3. The crystal structure was refined to $R(I/\sigma(I) > 4)$ of 3.45% and $wR2$ of 8.52% (S.G. $P2_1/m$). The displacement parameters are unusually large as consistent with positional disorder. Ca and REE are partitioned between the A1 and the A2 sites, Fe^{2+} between the M3 and the A1 sites, and Fe^{3+} between the M3 and the M2 sites. Th is confined to A1. The Mössbauer spectrum implies the presence of five different iron sites, three of which are attributed to Fe^{2+} at the M3 site, one to Fe^{2+} at the A1 site, and one to Fe^{3+} at a rather distorted octahedral site.

Annealing at 700 °C caused contraction of cell edges (b and c shrank by 0.5%, a by 0.3%, β only slightly decreased; ~1% in V) and of bond distances, with a consequent overall increase in bond valences. Displacement parameters decreased by about 30%, leading to a significant increase from 1495 to 1627 in the number of reflections with $I/\sigma(I) > 4$. Structure rearrangement was achieved by means of flexible points such as the two-coordinated oxygen atoms O8 and O9, and by greater volume decreases in M3, A1, A2, and Si3 polyhedra. Si tetrahedra behaved non-rigidly, at variance with what was observed for isomorphous substitution and thermal expansion.

Despite the high Th content and the age of the mineral, the crystal structure is well preserved. The above paradox could be explained by a thermal event after formation of the mineral that reversed previous damage, or by a prolonged period under relatively high-temperature conditions.

Keywords: Crystal structure, dissakisite-(La), Mössbauer spectroscopy, new minerals, high-temperature studies