

Poster Presentations

[MS18-P11] Symmetry, Cation Ordering and Diffuse Scattering in Labuntsovite-Group Minerals.

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The labuntsovite-group minerals (LGMs) are natural microporous titanates with open Ti-Si octahedral-tetrahedral frameworks. Crystal chemistry of LGMs is of interest due to their chemical and structural diversity [1]. Cation ordering and diffuse scattering of LGMs have been a subject of several studies that allowed to understand basic features of their structural origin [2, 3, 4]. Ideal symmetry of octahedral-tetrahedral framework of the LGM is described by the space group $Cmmm$, however, there is only one synthetic member of the group, where the $Cmmm$ $Cmmm$ has been realized [5]. All known minerals of the labuntsovite group can be divided into two subgroups according to their symmetry: monoclinic and orthorhombic members. Orthorhombic members have $Pbam$ symmetry which can be obtained from the ideal symmetry by removal of a number of symmetry elements of symmetry without the change in unit-cell parameters. The symmetry reduction is due to the electron-driven distortion of the octahedral coordination of titanium. Monoclinic members are described in terms of the space group $C2/m$. Unit-cell transformation from $Cmmm$ ($\mathbf{a}_i, \mathbf{b}_i, \mathbf{c}_i$) to $C2/m$ ($\mathbf{a}', \mathbf{b}', \mathbf{c}'$) can be described as follows: $\mathbf{a}' = 2\mathbf{a}_i, \mathbf{b}' = 2\mathbf{c}_i, \mathbf{c}' = \frac{1}{2}(\mathbf{a}_i + \mathbf{b}_i)$. In addition, there are monoclinic LGMs with the doubled c parameter with two possible space groups: $C2/m$ or $I2/m$ ("ordered labuntsovite"). The concurrent substitutions at the C and D sites with a $C-D$ distance of 2.1–2.2 Å is a key feature of the structure of monoclinic LGMs. The C site may be occupied by water molecules or large cations ($\text{K}^+, \text{Ba}^{2+}$, etc.), whereas the D site possess an octahedral coordination and can be occupied by

cations, such as $\text{Mg}^{2+}, \text{Mn}^{2+}, \text{Fe}^{2+}$, etc. The first example of cationic $C-D$ ordering, which is accompanied by splitting of C and D sites into different (in occupancy) sites $C1-C2$ and $D1-D2$, was reported in 2006 [2]. The $C1-D1$ and $C2-D2$ pairs are antagonistic, and only one site may be occupied by cations in a single unit cell. The $C-D$ ordering results in formation of superstructures, that are detected by the presence of weak Bragg reflections. At the same time analysis of diffuse scattering features allows to understand the degree of $C-D$ ordering, i.e. the relative size of ordered domains [6]. The $C-D$ ordering results in formation of chessboard-like arrangements in the ab plane, where the black and white squares correspond to C - and D - occupied units (parts of the unit cell). In completely ordered structure, the chessboard-like arrangements alternate along the \mathbf{c}^* axis, so the white squares are overlaid by black squares, and vice versa. Thus the completely ordered labuntsovite ($I2/m$ cell with the doubled c parameter) will have CDCD arrangement along \mathbf{c}^* -axis. Within the ab plane, each C block share edges with four adjacent D blocks and vice versa. The degree of correlation between the C and D blocks defines formation of superstructures and the appearance of diffuse scattering features. When there is no block correlation in the ab plane, the structure is completely disordered.

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