

# Symmetry, Cation Ordering and Diffuse Scattering in Labuntsovite-Group Minerals

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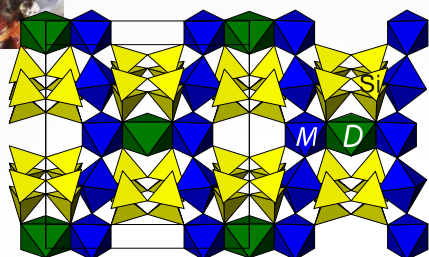


Fig. 1. Crystal structure of LGMs

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  $Cmmm$  has been realized [5]. All known minerals of the labuntsovite group can be divided into two subgroups: monoclinic and orthorhombic members. Orthorhombic members have  $Pbam$  symmetry, monoclinic members are described in terms of the space group  $C2/m$ . Unit-cell transformation from  $Cmmm$  ( $a_i, b_i, c_i$ ) to  $C2/m$  ( $a', b', c'$ ) can be described as follows:  $a' = 2a_i, b' = 2c_i, c' = \frac{1}{2}(a_i + b_i)$ . In addition, there are monoclinic LGMs with the doubled  $c$  parameter with two possible space groups:  $C2/m$  or  $I2/m$  ("ordered labuntsovite") (fig. 2).

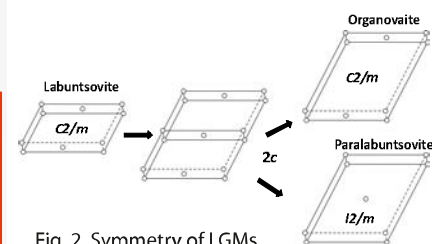


Fig. 2. Symmetry of LGMs

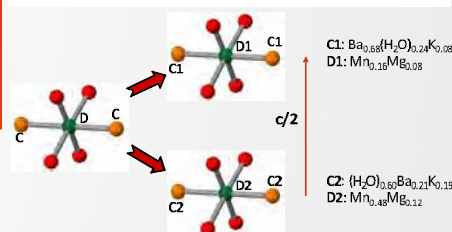


Fig. 4. High degree of C-D ordering

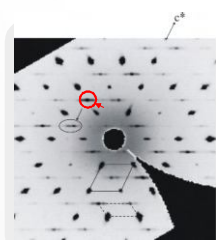


Fig. 3. Weak reflections of LGMs superstructure

The C-D ordering results in formation of superstructures, that are detected by the presence of weak Bragg reflections (fig. 3). 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].

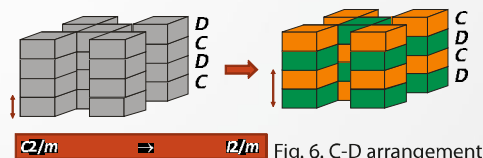


Fig. 6. C-D arrangement

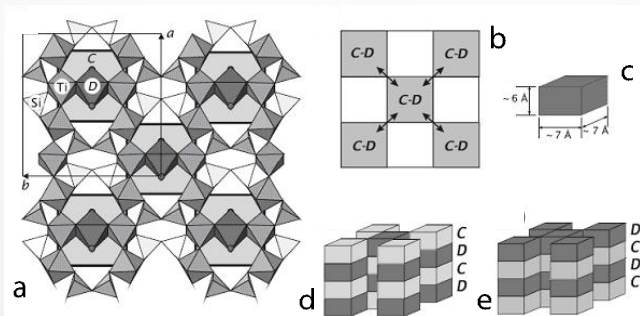


Fig. 5. a - ab plane C-D units; b - chessboard-like arrangements; c - size of one C-D unit; d - completely ordering; e - C-D partially ordering.

The C-D ordering results in formation of chessboard-like arrangements in the  $ab$  plane (fig. 5), 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  $c^*$  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  $c^*$ -axis. Within the  $ab$  plane, each C block share edges with four adjacent D blocks and vice versa (fig. 6). The degree of correlation between the C and D blocks defines formation of superstructures and the appearance of diffuse scattering features (fig. 7, 8). When there is no block correlation in the  $ab$  plane, the structure is completely disordered. Diffuse scattering in ordered labuntsovite is due of partial loss of the correlation between adjacent C-D sites

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 ( $K^+$ ,  $Ba^{2+}$ , etc.), whereas the D site possess an octahedral coordination and can be occupied by cations, such as  $Mg^{2+}$ ,  $Mn^{2+}$ ,  $Fe^{2+}$ , etc.. The C1–D1 and C2–D2 pairs are antagonistic, and only one site may be occupied by cations in a single unit cell. (fig. 4).

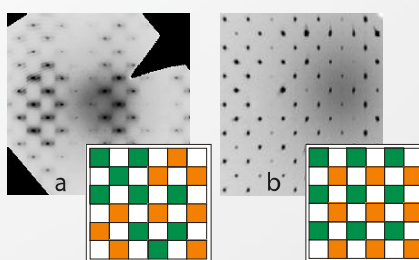


Fig. 7. Correlation between the C and D blocks: a- partially ordered; b- completely ordered.

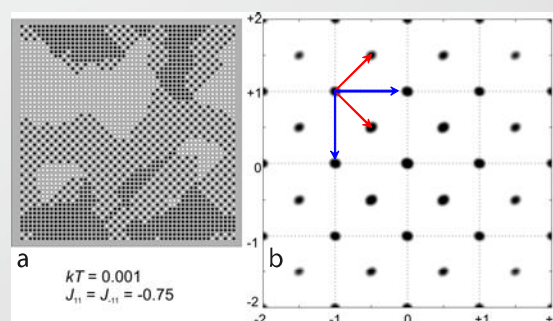


Fig. 8. a- correlation corresponding to C-D ordered labuntsovite; b- additional superstructure reflections on the diffraction pattern. Using DISCUS (<http://discus.sourceforge.net>) for simulation.

[1] Chukanov N. V., Pekov I. V., Zadov A. E., et al., Minerals of the Labuntsovite Group. Nauka, Moscow. (2003). [in Russian]. 323.

[2] Zolotarev A. A. Jr., Krivovichev S. V., Yakovenchuk V. N., Pakhomovsky Ya. A., Organova N. J., Armbruster T. Doklady Earth Sciences. (2006). Vol. 410, No. 7. 1062–1065.

[3] Armbruster T., Krivovichev S. V., Weber T., Gnoss E., Organova N. N., Yakovenchuk V. N. Amer. Mineral. (2004). Vol. 89. 1655–1666.

[4] Organova N. J., Krivovichev S. V., Zolotarev A. A., Shlyukova Z. V. Minerals as Advanced Materials I. Springer, Heidelberg. (2008). 72–77.

[5] Cadoni M., Ferraris G. (2007) Eur. J. Mineral. Vol. 19. P. 217–222.

[6] Krivovichev S. V., Zolotarev A. A. Jr., Spiridonova D. V., Yakovenchuk V. N. Typomorphic minerals and mineral associations - indicators of the magnitude of natural and man-made deposits and ore quality. (2008). 52–55.