1. Introduction

Barrier et al. [1] discovered a new structure type in Sr$_3$NiF$_6$O$_3$, which they described as an intergrowth between the brownmillerite and the K$_2$NiF$_4$ structures. To the best of our knowledge no other structures of this type are known until now.

In contrast to brownmillerites $(\lambda_3\beta_4\delta_5\Omega_6)$, which exhibit a three-dimensional framework of octahedrally and tetrahedrally coordinated $\beta$ cations — this structure type shows only slabs $(O-T-O)$ of the brownmillerite framework (Fig. 1).

Because of the close relation to the ‘true’ brownmillerites, we suggest the term layered brownmillerite for this class of materials. A general formula can be given as $\lambda_3\beta_4\delta_5\Omega_6$. In Sr$_3$NiF$_6$O$_3$, the $\lambda$ sites are occupied by Sr$^{2+}$ and Nd$^{3+}$, the $\beta$ sites by Fe$^{3+}$ only.

The structure can be described in space group Amma (the non-standard setting is used to match with the standard setting used for brownmillerites: $a$ along the tetrahedral chains, $b$ perpendicular to the stacking direction). Separated brownmillerite blocks are stacked along $c$. Each block is made up from three layers: octahedral-tetrahedral-octahedral. The structural model in Amma requires disorder of right- and left-handed tetrahedral zweier single chains. The $\beta$ cations are located in interstitial voids.

3. Manganese-containing ferrites

The system Ca$_3$Fe$_2$O$_4$-$\delta$-Ca$_3$Mn$_2$O$_4$-$\delta$-Ca$_3$Al$_2$O$_4$-$\delta$ was investigated by many authors (see Zölit & Pollmann [2] and citations therein), due to its relevance for the chemistry of cements. Single-crystal growth experiments of manganese-containing brownmillerites using a flux of Ca$_2$O$_3$ [3] produced crystals of the layered brownmillerite structure type. If the $\lambda$ sites are occupied by Ca, the $\beta$ cations have to sum up to a charge of ten. If three and four-valent species are considered, one third of the $\beta$ type cations have to exhibit oxidation state 4+.

By variation of the composition of the starting materials, we successfully synthesised single crystals of layered brownmillerites in the following systems:

- Ca$_3$(Fe$_{\delta}$Mn$_{\lambda}$)$_3$O$_9$
- Ca$_3$(Fe$_{\delta}$Mn$_{\lambda}$)$_3$Ti$_3$O$_9$
- Ca$_3$(Al$_{\delta}$Fe$_{\lambda}$Mn$_{\lambda}$)$_3$O$_9$
- Ca$_3$(Al$_{\delta}$Fe$_{\lambda}$)$_3$Ti$_3$O$_9$

An electron Microprobe analysis of the manganese-containing alumino-ferrites, shows that one third of the $\beta$ site cations are manganese. Chemical analysis of the other compounds are currently performed. Another open question is a possible non-stoichiometry.

4. Diffuse scattering

All investigated samples of the manganese-containing layered brownmillerites show strong diffuse scattering in the diffraction pattern. The diffuse intensity is located in rods parallel to the stacking direction $(h0l)$. These rods are well separated from the lattice of Bragg reflections. Figure 2 illustrates the orientation of the diffuse intensities in the reciprocal space.

Their arrangement suggest that the tetrahedral chains (left- and right-handed) are not randomly disordered within the layers, as required by the space group Amma, but show an alternating sequence along $c$. This is supported by the fact, that the diffuse scattering is located at $1/4$ values, doubling the $c$ lattice constant.

In the Amma structure a centring vector of $[0 \ \pm \quad \pm \ \pm]$ relates neighbouring tetrahedral sheets. Considering an alternating sequence of the chains (and consequently a doubled $c$ lattice constant) this centring vector becomes $[0 \ 1/2 \ 1/2]$. However, applying the $-2$ shift to the other direction $[0 \ 1/2 \ 1/2]$ gives a second option for the neighbouring layer (see Figure 3). As a result, the alternating chain sequence allows stacking faults.

However, these stacking faults cannot be the only mechanism of disorder, because they do not explain the observed intensity distribution along the diffuse streaks. As can be seen in Figure 4, they show pronounced maxima and minima of their intensities, with a periodicity which is much larger than the reciprocal lattice vector $1/4'$. The underlying disorder will be the target of future investigations.

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References

[2] M. Zölit & H. Pollmann (2006), Stability and properties of brownmillerites $\text{Ca}_3(\text{Al}_{1-x}\text{Fe}_x)\text{O}_4$, $\text{Ca}_3(\text{Al}_{1-x}\text{Mn}_x)\text{O}_4$ and pseudobrookites $\text{Ca}_3(\text{Al}_{1-x}\text{Ga}_x)\text{O}_4$. Journal of the American Ceramic Society 89(11), 3491-4000, doi:10.1111/j.1551-2916.2006.01342.x