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Bi₂M₄O₉ compounds are known to have potential as electrolytes in solid oxide fuel cells (SOFC) [1]. The conducting properties could be related to an increased number of oxygen vacancies due to the requirement of charge neutrality with the substitution of Bi³⁺ by Sr²⁺ [2]. The samples were synthesized using the glycerin method as described in [3] and finely washed with nitric acid to remove impurity phases. Two different heating procedures were used for samples having an initial Sr content of $x = 0.2$. Heating steps of 353 K (1/2 h), 473 K (1/2 h) and 1023 K (2h) were used for one sample (#173) and the strontium free reference (#174), whereas the faster heated sample (#172) was treated at 473 K (1/4 h) and 1023 K (2h). The unit-cell volumes calculated from X-ray powder diffraction data of all samples calculated against silicon as internal standard show only a very small variation around $357.3(5) \cdot 10^{-6} \text{ pm}^3$. Whereas small amounts of Bi₂O₃ and SrAl₄O₉ were found in the as synthesized samples no indication for these impurities were detected in the washed samples. To prove the incorporation of Sr into the mullite-type structure small crystals of a sample with an initial Sr content of $x = 0.2$ (#172) were selected in a HRTEM. Suitable crystallites were analyzed by EDX in a scanning TEM mode using a spot size of approximately 300 pm. Several particles were evaluated showing a variation of x between 0.05 (often) and 0.24 (rare). A line scan on a crystal having a high Sr content ($x = 0.244$) shows homogeneous strontium distribution. If strontium is incorporated into the Bi₂Al₄O₉ structure two possibilities for charge balance have to be discussed. On one hand oxygen deficiency with vacant oxygen positions are possible. On the other hand for incorporating 2 Sr²⁺ ions 1 Bi³⁺ could be oxidized to Bi⁵⁺. To exclude the latter possibility XPS investigations were carried out on two samples with $x = 0.2$ (#172, #173) and Bi₂Al₄O₉ (#174) and Bi₂O₃ as references. No indication was found that Bi⁵⁺ is formed during the strontium incorporation. Nevertheless, for the fast synthesized sample (#172) the Bi4f photoelectron peaks are much more asymmetric than in the slowly synthesized compound (#173). X-ray powder heating experiments between 298 K and 1272 K for Bi₂Al₄O₉ show a (nearly) linear thermal expansion in all three orthorhombic lattice directions without any changes during the heating and cooling runs. For the strontium doped samples an irreversible deviation for the thermal expansion was observed at ~1085 K (#172) and ~1135 K (#173) for the as synthesized and at ~1185 K for both washed samples. Adding 15 wt-% Bi₂O₃ to the latter sample (#173) the expansion deviation was observed at ~1035 K. In all cases the refined (Rietveld method) strontium content on the bismuth position was reduced from 15(3)% to zero at these temperatures.

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FA2-MS16-P28

Polytypism in Na[C₆H₄Cl(SO₃)]·H₂O analysed by Order-Disorder (OD) Theory. Jürgen Glinnemann,

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Ordered and disordered crystal structures of the title compound are built up by two chemically rather distinct kinds of alternating layers: (1) hydrophilic NaSO₃(H₂O), and (2) hydrophobic C₆H₄Cl layers [1].

The hydrophilic layers are ordered and act like templates on the hydrophobic layers. Due to this steric condition, the C₆H₄ rings have to be mutually perpendicular aligned in their respective layers. These have an orthogonal metric with layer-group symmetry *C1m1*, layer orientation (001). The ability for different stacking sequences of these layers gives rise to a family of structures, ordered and disordered ones. Their discussion will follow the lines of order-disorder (OD) theory [2, 3], and starts with the OD groupoid family symbol:

$$C \ 1 \ m \ (1) \\ \left\{ \begin{array}{l} 1 \ 2_s \ 1 \\ 2_r \ 1 \ n_{r,s} \end{array} \right\}$$

The OD approach results in three maximum degree of order (MDO) polytypes and in the disordered family structure, all structures consisting of four layers (1) and (2) in their respective unit cells. Two of the MDO structures have space-group type *P12₁/c1* ($Z = 8$) (layer orientation (010)) with the same lattice parameters. The third MDO structure has space-group type *C1c1* ($Z = 16$), with an orthogonal metric (layer orientation (001)). The disordered family structure ('average structure') is orthorhombic, space-group type *Pnma* ($Z = 4$) (layers parallel (100)).

One of the MDO '*P2₁/c* polytypes' could be identified by X-ray single-crystal analysis, yet with severe disorder, as exemplified by streaks of diffuse scattering in direction perpendicular to the structural layers [1]. Moreover is this structure twinned, the twin laws reflecting the two mirror planes of the point group of the orthorhombic family structure perpendicular to the layers.

In addition to the three MDO polytypes and the disordered family structure, all with a periodicity of four layers, less-ordered structures with larger periodicities or disordered ones without any stacking periodicity may occur. Altogether these polytypes establish the OD family of structures of the title compound.

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RT and high T crystal structure of ferroelastic

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