THE NON-STOICHIOMETRIC PEROVSKITE $BAPBO_{3-x}$: CRYSTAL STRUCTURE AND CATION - ANION DISTRIBUTION

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The ABO_3 perovskites reveal a large structural tolerance for enabling a variety of substitutions at both A and B sites and for a wide range of cation and vacancy ordering. This led to a number of discoveries of useful chemical and physical properties.
In particular the oxygen deficit influences the electrical conductivity of ABO_3 perovskites. The degree of oxygen deficiency is influenced by sample preparation, calcination temperature and atmosphere used for synthesizing and annealing. However, oxygen measurements are challenging and the references give either none or incorrect data. Finally, conclusions described in literature about the structure of $BaPbO_3$ are contradicting with respect to the oxygen content.
Describing the structure, the most suggested space groups in references for $BaPbO_{3-x}$ are either the monoclinic space group I2/m [1-3] or the orthorhombic space group Imma [4, 5]. Imma as well as I112/m show tilted PbO_6 octahedra around the [100] - and [010] - axis of the cubic aristotype. Although the tilt angle for Imma equals for a- and b-axis, it is different in I112/m. If differences between tilt angles are small a structural classification is rather difficult.
The synthesis of homogeneous $BaPbO_{3-x}$ powder samples with a defined oxygen amount takes place through the combination of a main synthesis and secondary treatment: oxalates were homogenized dry as well as in an aqueous suspension followed by calcination in air using an optimized temperature profile (up to 850°C). Afterwards the perovskites were annealed in vacuum, air and oxygen atmosphere as well as at different temperatures (up to 800°C) which corresponds to different oxygen fugacity. The variation of homogenization methods yields homogenous powder samples with various oxygen deficiencies (x=0.5(1) - 0.1(1)) up to fully occupied anion sites ($BaPbO_3$).

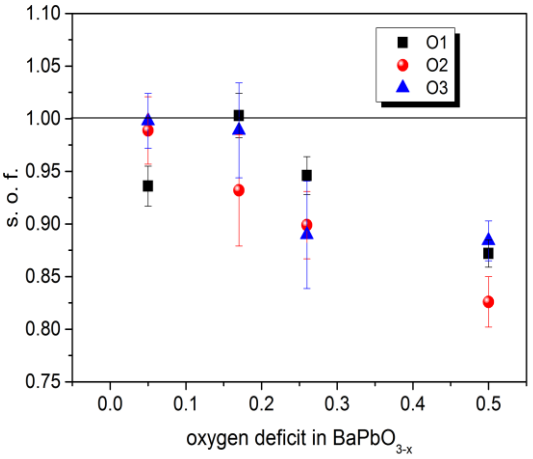

Figure 1 – anion distribution with respect to oxygen deficiency in $BaPbO_{3-x}$

The oxygen content was analysed by Temperature Programmed Reduction. The hydrogen consumption during the reduction of tetravalent lead to Pb^0 was used to calculate the degree of the oxygen deficiency and revealed as well Pb^{2+} as Pb^{4+} as part of the crystal structure.
Neutron powder diffraction experiments at room temperature were performed using the fine resolution powder diffractometer E9 at Helmholtz-Zentrum Berlin für Materialien und Energie (Berlin, Germany). The presentation will give an overview of the Rietveld refinement results with focus on the oxygen distribution at the three different Wyckoff positions (4i, 4g, 4h) with respect to the amount of oxygen deficit (see fig.1). Furthermore, the distribution of Pb^{2+} and Pb^{4+} on the A- and B- sites are discussed.

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