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Single-crystal growth and characterization of mullite-type $\text{Bi}_2\text{Me}_4\text{O}_9$ (Me=Ga,Al). Jan Ottinger^a, Manfred Mühlberg^a, Manfred Burianek^a, Hartmut Schneider^a, Justus Tonn^b, Andreas Danilewsky^b, Detlef Klimm^c. ^a*Institute for Crystallography, University Cologne, Germany.* ^b*Crystallography, Institute for Geoscience, Albert-Ludwigs-University Freiburg.* ^c*Leibniz Institute for Crystal Growth, Berlin.*
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The bismuth metal oxides ($\text{Bi}_2\text{Me}_4\text{O}_9$ (Me=Ga,Al,Fe)) crystallize in the space group Pbam ($a_1 = 7.929\text{\AA}$, $a_2 = 8.295\text{\AA}$ and $a_3 = 5.893\text{\AA}$ for $\text{Bi}_2\text{Ga}_4\text{O}_9$). They have a mullite-type structure with edge-linked $[\text{MeO}_6]$ -octahedron chains, which are alternating linked with $[\text{Me}_2\text{O}_7]$ -groups from corner-linked $[\text{MeO}_4]$ -tetrahedron and $[\text{BiO}_6]$ -groups. It was expected, that this structure should be capable of incorporation divalent cations like Sr^{2+} or Ca^{2+} for increasing ionic conductivity. Thereby, these materials are assumed to apply in oxygen-hydrogen fuel cells. Zha et al. [1] found such increased conductivity in Sr^{2+} -doped $\text{Bi}_2\text{Al}_4\text{O}_9$ ceramics samples.

The aim of this paper was the growth of doped and undoped crystals and an investigation of the bulk crystal properties [2]. Because of incongruent melting at 1082°C the Top Seeded Solution Growth (TSSG) method was used. Single-crystals with $\langle\text{cm}^3\rangle$ -dimension are grown with the orientation $\parallel [001]$ from solution of about 100 ml. Depending on chemical composition the starting temperatures are between 1050°C and 850°C , the cooling rates are in the range of 3-6 K/d.

Steep liquidus line and limited solubility of Al_2O_3 in Bi_2O_3 is the reason why only small $\text{Bi}_2\text{Al}_4\text{O}_9$ -crystals can be obtained. Free from inclusions and clear-transparent crystals with (001)-faces and dominant $\{110\}$ -faces can be grown especially from $\text{Bi}_2\text{Ga}_4\text{O}_9$.

Sr^{2+} and Ca^{2+} doped $\text{Bi}_2\text{Ga}_4\text{O}_9$ single-crystals show only a doping level in the range of about 150-200 ppm, which was determined by electron micro probe analysis. Contrary to ceramic samples a higher oxygen ionic conductivity could not be observed.

On selected $\{110\}$ - and $\{001\}$ -surfaces a rocking curve mapping was made to get details about the structural quality and homogeneity. It was realized with a high resolution x-ray diffractometer with Ge (220) double-crystal-monochromator. On the entire surface the FWHM of the 220-reflex varies between $33.8''$ to $53.9''$ and the FWHM of the 002-reflex between $31.6''$ to $48.5''$.

The refractive indices dispersion of $\text{Bi}_2\text{Ga}_4\text{O}_9$ was determined by the prism method: at 580 nm: $n_{\alpha\parallel a_3} = 2.089(2)$, $n_{\beta\parallel a_1} = 2.113(2)$ and $n_{\gamma\parallel a_2} = 2.172(1)$, the birefringence is $\Delta n_{\text{max}} = 0.086(6)$; the optical character is 2+ with $2V_{\gamma} = 64.80^\circ$.

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[1] Zha, S.; Cheng, J.; Lui, Y.; and Meng, G., *Solid State Ionics*, 2003, 156, 197. [2] Burianek, M.; Mühlberg, M., Woll, M. et. al., *Cryst. Res. Technol.*, 2009, 44, 1156.

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New synthetic cyclosilicates as potential Li/Na-ionic conductors. So-Hyun Park^a, Carola J. Pietsch^a, Ismot F. Akter^a, Julien Labbe^a, Lucy B. Garcia^a, Carsten Paulmann^b, Anatoliy Senyshyn^c, Markus Hoelzel^c. ^a*Section Crystallography, Dept. Earth and Environmental Sciences, Ludwig-Maximilians-Universität München, Germany,* ^b*Mineralogisch-Petrographisches Institut Universität Hamburg, Germany,* ^c*Materials Science, Technical University Darmstadt, Germany.*
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Li-Na-bearing cyclosilicates are of interest as ionic conductors, based on our previous studies on several natural compounds, such as sogdianite, sugilite, pezzottaite, and emeleusite [1-4]. A direct current conductivity value of $\sim 1 \times 10^{-3} \text{ S cm}^{-1}$ at $T = 1093 \text{ K}$ was estimated with impedance spectra of sugilite, the best cationic conductor among this type materials, reported so far. However this conductivity value is desired at room temperature in order to realize industrial application. Nonetheless, a crystal-chemical basis for the formation of solid-solutions and defect-engineering with sugilite-type materials, encourages to simplify the system of its natural constituents and, more importantly, to improve the ionic conductivity, as well as to introduce the mixed conductivity in its 2-dimensional network of $\text{LiO}_4\text{-FeO}_6$. Recently, it is successful for us to synthesize an end-member of sugilite via hydrothermal route, for the first time. Its structural and electrochemical properties will be present at ECM 2010. On the other hand, we are interested in another cyclosilicate, willemite (Zn_2SiO_4) for an extremely wide stable range on the synthesis and its intrinsic chemical stability, while pursuing to find a chemically much simple system of materials desirable for all-solid-state Li-ionic batteries. Recently we have synthesized a new willemite-type compound containing Li/Na cations in its six membered-ring (6MR) channels [5]. The presence of non-framework alkali metal cations within the 6MR-channels of a willemite-type structure is new to its numerous variants reported so far. Our investigation using Rietveld-Analysis with X-ray and neutron diffraction powder data and electron microprobe confirm the presence of Li/Na cations within the channel. We present here very recent results from crystallographic investigation on local and long-range site-exchanging processes of Li^+ in this compound. Our finding suggests this material as a new prototype for Li-/Na-ionic conductors exhibiting the stable willemite topology.

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