Experimental report

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Proposal: 5-21-1156 **Council:** 4/2020

Title: Nitrogen Order in Inverse Perovskites

Research area: Chemistry

This proposal is a new proposal

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Samples: (Ca3Nx)Pb
(Ca3Nx)Ge
(Ca3Nx)Sn
(Ba3Nx)Ge
(Ca3Nx)Si

Instrument	Requested days	Allocated days	From	To
D2B	3	3	19/02/2021	22/02/2021
D20	1	0		

Abstract:

The inverse perovskites (Ca3Nx)Ge, (Ca3Nx)Sn and (Ca3Nx)Pb were first reported in 1992 to crystallize in the perovskite aristotype space group Pm-3m with full occupation of the nitrogen site. Our samples have a lower nitrogen content and show superstructure reflections indicating an elpasolite-type ordering of the nitrogen site, leading to space group Fm-3m. However, this ordering can only indirectly be observed using X-ray diffraction due to the low electron count of nitrogen. We only see the shift of the surrounding calcium atoms (nitrogen containing NCa6 octahedra are smaller than 'empty' ones). In addition, we have synthesized samples of the new inverse perovskites (Ca3Nx)Si and (Ba3Nx)Ge, the latter of which is distorted due to octahedral tilts in addition to the elpasolite superstructure. We would like to conduct neutron diffraction experiments at D2B to clearly identify if there is full or partial ordering of the nitrogen site. These experiments should include low temperature measurements for (Ca3Nx)Si and (Ca3Nx)Ge, as well as a high temperature measurement at D20 for (Ba3Nx)Ge to detect additional distortions.

We are investigating the crystal structure and properties of inverse perovskite nitrides with an elpasolite-type superstructure. This superstructure is due to a full or partial ordering of nitrogen atoms and defects on the perovskite B site. Neutron diffraction measurements of four compounds showing this superstructure, $(Ca_3N_x)Ge$, $(Ca_3N_x)Sn$, $(Ca_3N_x)Pb$ and $(Ba_3N_x)Ge$, were performed at D2B in february. Before this, we had illuminated their crystal structures using lab-scale X-ray powder diffractometry, but were unable to determine the exact nature and extent of the superstructure.

Using neutron diffraction, we were able to model the superstructure much more reliably for each compound. The neutron diffraction data is commensurate with the X-ray measurements. This allowed for mixed pattern Rietveld refinements, utilizing the advantages of both methods. However, the data gathered from $(Ca_3N_{0.56})Pb$ and $(Ba_3N_{0.5})Ge$ are of lesser quality, which can at least in part be explained by the smaller sample size. For $(Ba_3N_{0.5})Ge$, a full ordering of the nitrogen site was confirmed, which was earlier also observed for the related compounds $(Sr_3N_{0.5})Ge$, $(Ba_3N_{0.5})Sn$ and $(Ba_3N_{0.5})Pb$. In contrast, the compounds containing calcium have a higher nitrogen content and show only partial ordering. In all cases, the site at (0, 0, 0) is fully occupied by nitrogen. In addition, we were able to confirm our structural models suggesting octahedral tilting leading to an inverse $Na_3[AlF_6]$-type structure for $(Ca_3N_{0.69})Ge$ and $(Ba_3N_{0.5})Ge$ and an inverse $K_2(NaAlF_6)$-type structure for $(Ca_3N_{0.65})Sn$ and $(Ca_3N_{0.56})Pb$.

The measurements at low temperatures did not indicate any phase transitions towards lower symmetry crystal structures. Apart from some tiny additional peaks which could be ascribed to frozen argon, no changes were observed when comparing to the room temperature measurements. The same was true for the high temperature measurements, which unfortunately had to be restricted to 120 °C due to practical concerns.

These results will also enable us to model the band structure of these compounds. We plan to publish our findings along with other inverse perovskite nitrides in the first half of 2022.