Experimental Report

Proposal: **5-23-663** **Council:** 4/2014

Title: The structure investigation of SrMo1-xWx(O,N)3 solid solution perovskite oxynitrides

This proposal is a new proposal

Researh Area: Materials

Main proposer: **LI Wenjie**

Experimental Team: LI Wenjie

Local Contact: SUARD Emmanuelle

Samples: SrMo(1-x)WxO2N

Instrument	Req. Days	All. Days	From	To
D2B	3	2	29/09/2014	01/10/2014

Abstract:

Perovskite oxynitrides represent an emerging class of materials suitable for novel applications in the fields of energy conversion, storage and so on. Nitrogen substitution for oxygen allows for the stabilization of compositions that are not achievable for perovskite oxides and can be applied to change the concentration of charge carrier and consequently the electronic and magnetic properties. Till now, nothing is known about the solid solution phase of molybdenum and tungsten-contained perovskite oxynitrides, even both SrMo(O,N)3 and SrW(O,N)3 have been studied in recent years. Therefore, the solid solution of SrMo1-xWx(O,N)3 arise lots of interesting to figure out the structure information and furthermore potential promising properties.

The Structure Investigation of novel $SrMo_{1-x}W_x(O,N)_3$ Solid-Solution Perovskite Oxynitrides

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The novel $SrMo_{1-x}W_x(O,N)_3$ perovskite-type oxynitrides were successfully synthesized and structure was resolved via neutron diffraction performed at D2B-ILL with λ= 1.6 Å. We found the perovskite-type solid-solution oxynitrides formed for the selected samples (when x=0.15(SMW2), 0.75(SMW7) and 0.85(SMW8)) in terms of cubic Pm-3m phase, accompanying with retained oxide.

The synthesis of perovskite-type solid-solution $SrMo_{1-x}W_x(O,N)_3$ oxynitrides from their corresponding scheelite-type $SrMo_{1-x}W_xO_4$ oxide precursors might be of high interest concerning their formability, as well as electrical conductivity and magnetic properties, especially when $SrMo(O,N)_3$[1] and $SrW(O,N)_3$[2] have been explored in recent years.

The powder neutron diffraction experiment on polycrystalline samples of the title compounds were performed on the D2B high resolution powder diffractometer with λ = 1.6 Å.

The phase-pure scheelite-type oxides $SrMo_{1-x}W_xO_4$ (when x= 0.05, 0.15, 0.25, 0.4, 0.5, 0.6, 0.75, 0.85, 0.95) were achieved according to Rietveld refinement based on our Lab X-ray diffraction. The novel corresponding perovskite-type oxynitrides can be formed for our selected samples (when x= 0.15, 0.75 and 0.85).

Figure 1 shows the Rietveld refinement results. In case of SMW2, only less than half amount (45.8 wt%) of perovskite $SrMo_{0.85}W_{0.15}O_{2.15(6)}N_{0.85(6)}$ was formed and showed a slightly lower nitrogen content as compared to the other two samples (an unknown peak region was excluded). SMW7 did not show any decomposition upon preparation at 800 ^{0}C and yielded ca. 93 wt% of oxynitride phase ($SrMo_{0.25}W_{0.75}O_{1.77(4)}N_{1.23(4)}$). A higher ammonolysis temperature (800 instead of 700 °C) is required for SMW8 to obtain the oxynitride phase as main phase up to ~ 82.4 wt%. Interestingly, the formation of solid-solution seems to favor the nitrogen incorporation capability. Thus, in SMW8 the nitrogen content ($SrMo_{0.15}W_{0.85}O_{1.21(6)}N_{1.79(6)}$, O/N ratio 0.68, see Table 1) was significantly higher than that reported for $SrMoO_2N$ and $SrWO_{1.5}N_{1.5}$ [3] (O/N ratio of 2 and 1, respectively).

Table 1 Summarized Phase composition from refinement

Samples	Phase composition / wt %
SMW2 (x=0.15)	$SrMo_{0.85}W_{0.15}O_{2.15}N_{0.85}$ (45.79) + $SrMo_{0.85}W_{0.15}O_4$ (54.21)
SMW7 (x=0.75)	$SrMo_{0.25}W_{0.75}O_{1.76}O_{1.24}$ (92.87) + $SrMo_{0.25}W_{0.75}O_4$ (7.13)
SMW8 (x=0.85)	$SrMo_{0.15}W_{0.85}O_{1.21}O_{1.79}$ (82.43) + $SrMo_{0.15}W_{0.85}O_4$ (17.57)

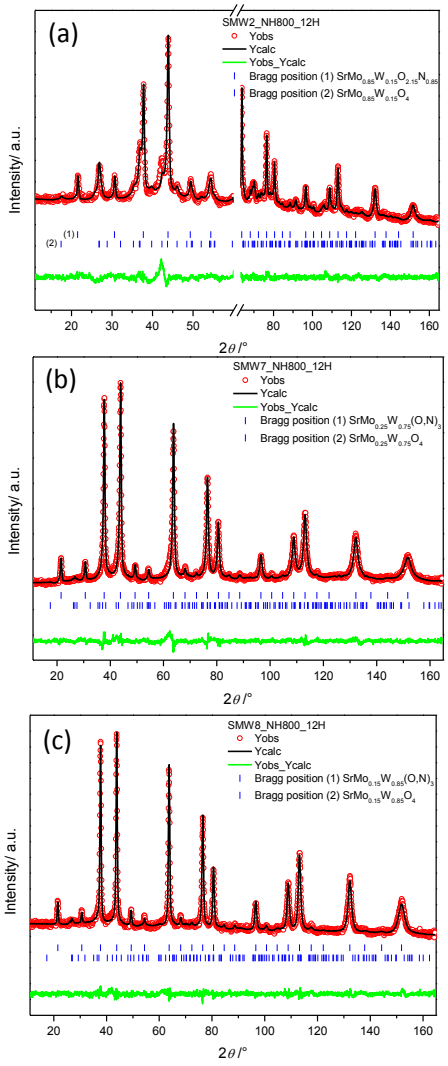

Figure 1 Rietveld refinement of the neutron diffraction pattern of the oxynitrides obtained after thermal ammonolysis at 800 °C for 12 h, (a) x=0.15, (b) x=0.75 and (c) x=0.85.

The manuscript has been submitted to **ZAAC** (Zeitschrift für anorganische und allgemeine Chemie).

[1] D. Logvinovich, *et. al., J Solid State Chem* 2007, *180*, 2649-2654.

[2] I. D. Fawcett, *et. al., Mater. Res. Bull.* 1997, *32*, 1565-1570.

[3] W. J. Li, *et. al., submitted* 2015.

Work partially performed at ILL supported by Dr. S. Emmanuelle
Proposal-number: 5-23-663
Instruments: D2B