Local structure of mixed metal Nb based oxynitrides \((\text{Nb},A)_x(O,N)_y (A = \text{Sr, Ni})\)

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1 Introduction

Niobium oxynitride doped with main group elements of Mg, Al and Si were recently found out to crystallize in rock salt structure [1]. They showed superconducting behavior below ~17 K. Magnesium oxide MgO crystallizes in rock salt structure as the superconducting \(\delta\)-NbN. On the other hand, partial substitution of silicon oxide SiO\(_2\) for the niobium nitride introduced cationic vacancy in the rock salt type lattice. X-ray absorption spectroscopy for the niobium K-edge was studied on the rock salt type niobium oxynitrides. Fourier transform of EXAFS spectra showed the first and second nearest neighbors around Nb at around 0.17 nm and 0.27 nm, respectively, for all samples. The peak profile was broader in the niobium oxynitride doped with silicon oxide than in the other oxynitrides. Silicon oxide might cause a relatively large displacement from ideal octahedral 4a site in the rock salt structure. Both nickel and strontium oxide also crystallize in rock salt structure NiO and SrO, respectively. Ionic radius of Ni ion is similar to that of Mg ion. In this study, nitridation of niobium oxide coexistent with nickel and the local structure around the niobium atom was investigated.

2 Experiment

\(\text{NbCl}_5\) was dissolved with \(\text{Ni(NO}_3\)\(_2\)-6H\(_2\)O in a molar ratio of \((1-x):x, x = 0.0\) and 0.1, in 20 mL of anhydrous ethanol in which an equimolar amount of citric acid was added as a complexing agent. The viscous gel was fired at 600 °C for 7 h and then nitrided at 800 °C and 1300 °C for 10 h under NH\(_3\) flow of 50 – 100 mL/min as reported in Ref. [1].

Crystalline phases were characterized using powder x-ray diffraction (XRD). X-ray absorption of Nb and Ni K-edges were measured in transmission mode at the beam line NW-10A and 9C, respectively, in Photon Factory. The spectrum was analyzed using REX2000 software [2].

3 Results and Discussion

Single phase of rock salt type niobium oxynitride was obtained by nitridation at 800 °C without Ni additive. Its second nearest neighbor around Nb is unclear in its Fourier transform compared with that for NbN reference. Anionic vacancy in the rock salt type Nb(O,N) induced at lower nitridation temperature decreased the crystallinity and disturbed the long range ordering as reported in Ref. [3]. Nb\(_2\)N\(_6\) secondary phase was observed with the rock salt type Nb(O,N) by nitridation with Ni additive at 800 °C, similarly to a nitridation of Fe-Nb oxide [4]. Its Fourier transform is different from that for Nb(O,N) obtained without Ni due to the formation of hexagonal Nb\(_x\)N\(_y\). The coexisting Ni was observed as Ni metal elucidated by XRD and XAFS studies. Higher nitridation temperature at 1300 °C transformed the rock salt type Nb(O,N) to hexagonal c-NbN irrespective of Ni additive.

![Fig. 1 Fourier transforms of the Nb K-edge EXAFS for niobium oxynitrides obtained at 800 °C without Ni (b), at 800 °C with Ni (c) and 1300 °C without Ni. That of rock salt type NbN reference is shown in (a).](image)

References


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