Crystal-structure and electron-density analyses of the perovskite-type oxynitrides BaNbO$_2$N and SrNbO$_2$N through synchrotron X-ray powder diffraction

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Crystal structure and electron-density distribution of the perovskite-type oxynitrides BaNbO$_2$N and SrNbO$_2$N have been analyzed by the synchrotron X-ray powder diffraction, Rietveld and maximum-entropy methods. In both BaNbO$_2$N and SrNbO$_2$N, the electron-density levels along the Nb–(O,N) bonds are significantly higher than those along the Ba–(O,N) and Sr–(O,N) bonds, which indicates higher covalency of the Nb–(O,N) bonds. The Nb–(O,N) bonds in SrNbO$_2$N have higher electron-density levels than that in BaNbO$_2$N, which suggests higher covalency of Nb–(O,N) bonds in SrNbO$_2$N. The higher covalency of SrNbO$_2$N cannot explain its wider band gap $E_g$ than $E_g$ of BaNbO$_2$N. The wider $E_g$ of SrNbO$_2$N compared to BaNbO$_2$N is attributable to the smaller Nb–(O,N)–Nb' angles of SrNbO$_2$N.

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Three independent interatomic distances of Sr in BaNbO$_2$N. This is ascribed to the smaller size of Sr$^{2+}$ of electron-density distributions along the Ba between these atoms. On the other hand, there is less connection electron-density distributions in BaNbO$_2$N and SrNbO$_2$N. In both number of twelve (1.44

BaNbO$_2$N (2.06415(1)  
interatomic distances are shorter than that of Nb  
BaNbO$_2$N (2.0228(8) Å).  

The tolerance factors were 2.776(15), 2.85558(2), and 2.946(15)  

Fig. 1. Rietveld patterns of synchrotron X-ray powder diffraction data of (a) BaNbO$_2$N and (b) SrNbO$_2$N. Red crosses and blue line denote the observed and calculated intensities, respectively. Black ticks and purple lines at the bottom represent the Bragg peak positions and difference profile between the observed and calculated intensities, respectively.

Fig. 2. Refined crystal structures of (a) BaNbO$_2$N, and (b) SrNbO$_2$N. SrNbO$_2$N has two independent (O,N) sites where the equatorial and apical (O,N) sites are labeled as (O1,N1) and (O2,N2), respectively.

2.919142(14) Å for Ba–(O,N) and 2.06415(1) Å for Nb–(O,N). Three independent interatomic distances of Sr–(O,N) in SrNbO$_2$N were 2.776(15), 2.85558(2), and 2.946(15) Å. The average interatomic distance of Sr–(O,N) 2.859 Å is shorter than Ba–(O,N) in BaNbO$_2$N. This is ascribed to the smaller size of Sr$^{2+}$ compared to Ba$^{2+}$. The ionic radius$^{35}$ of Sr$^{2+}$ with coordination number of twelve (1.44 Å) is smaller than that of Ba$^{2+}$ (1.61 Å). The interatomic distances of Nb–(O1,N1) and Nb–(O2,N2) were 2.02561(2) Å and 2.0228(8) Å, respectively, in SrNbO$_2$N. These interatomic distances are shorter than that of Nb–(O,N) in BaNbO$_2$N (2.06415(1) Å). This would also be due to smaller size of Sr$^{2+}$ compared to Ba$^{2+}$. The tolerance factor of SrNbO$_2$N 0.98 is smaller than that of BaNbO$_2$N 1.04. The tolerance factors of the previously known perovskite-type ABO$_2$N with space group Pm$n$3$m$ are between 0.99 and 1.04.$^{23}$ The lower tolerance factor of SrNbO$_2$N (0.98) can explain the lower symmetry of this material ($\Gamma$/mcm). There is an octahedral tilting of Nb(O,N)$_6$ in SrNbO$_2$N (a$^2$d$^2$c$^2$) in the Glazer’s notation$^{50}$).

The electron-density distributions of BaNbO$_2$N and SrNbO$_2$N were studied by the maximum-entropy method (MEM) using computer program Dysnomia.$^{51}$ Figure 3 shows the MEM electron-density distributions in BaNbO$_2$N and SrNbO$_2$N. In both cases, continuous electron-density distributions are observed along the Nb–(O,N) bonds, suggesting the covalent bonds between these atoms. On the other hand, there is less connection of electron-density distributions along the Ba–(O,N) and Sr–(O,N) bonds, which suggests their lower covalency. The minimum electron densities (MEDs) along the bonds were 0.62 Å$^{-3}$ for Nb–(O,N) in BaNbO$_2$N, 0.71 Å$^{-3}$ for Nb–(O1,N1), and 0.72 Å$^{-3}$ for Nb–(O2,N2) in SrNbO$_2$N. These are significantly higher than those of Ba–(O,N) or Sr–(O,N) bonds, which were between 0.25 and 0.30 Å$^{-3}$ (Fig. 3). The higher MEDs of

<table>
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<th>Atom</th>
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</table>

$^a$Crystal system: cubic, Space group: Pm$n$3$m$. Unit-cell parameters: $a = b = c = 4.12829(2)$ Å, $\alpha = \beta = \gamma = 90^\circ$. Reliability factors: $R_{exp} = 2.40\%$, $R_p = 1.63\%$, $R_B = 0.81\%$, $R_E = 0.61\%$.

$^b$Crystal system: tetragonal, Space group: $I4/mcm$. Unit-cell parameters: $a = b = 5.71115(4)$ Å, $c = 8.10243(6)$ Å, $\alpha = \beta = \gamma = 90^\circ$. Reliability factors: $R_{exp} = 1.22\%$, $R_p = 0.80\%$, $R_B = 0.78\%$, $R_E = 0.62\%$.
(O,N) in SrNbO$_2$N have more covalent character in SrNbO$_2$N than in BaNbO$_2$N. Therefore, SrNbO$_2$N is expected to have narrower band gap, because higher covalency generally leads to wider valence band width.\(^\text{15}\) On the contrary to the expectation, SrNbO$_2$N has wider band gap (1.95 eV) than BaNbO$_2$N (1.85 eV) as described before. The wider band gap of SrNbO$_2$N is attributable to the smaller Nb–(O,N)–Nb bond angles in SrNbO$_2$N (175.5° in average). A smaller Nb–(O,N)–Nb bond angle than 180° causes less overlap between (O,N) 2p and Nb 4d orbitals, which would result in smaller conduction band width and wider band gaps.\(^\text{16}\)

The valence band and conduction band, which determine the band gap, would be affected by Nb–(O,N)–Nb’ bond angle. In future, the investigation of the electronic structures might be necessary for further understanding of the correlation between the band gap and Nb–(O,N)–Nb’ angle. The synchrotron experiments were carried out on BL02B2 at SPring-8 (2016A1616) and on BL-4B2 at PF (2016G644, 2017G168). The neutron diffraction measurements were performed with the approval (2013B0178). This study was partly supported by a Grant-in-Aid for Scientific Research (KAKENHI, Nos. JP15H02291, JP25630365, JP26870190, JP16H00884, JP16H06293, JP16H06440, JP16H06438, JP16K21724, JP17H06222) from the Ministry of Education, Culture, Sports, Science and Technology of Japan and by the Asahi Glass Foundation.

References