Crystallography

4B2/2005G157, 2005G158, 2006G263, 2006G264

Crystal Structure and Electron Density of Apatite-type $Nd_{9.25}Si_6O_{25.88}$

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Introduction

Solid oxides that exhibit high ionic conductivity have attracted widespread interest in recent years owing to their technological importance in a number of applications, such as oxygen sensors, separation membranes and solid oxide fuel cells. From this point of view recently significant interest has been aroused in Si-based materials having apatite-type structure as they exhibit high oxide ion conductivities. Crystal structure and properties of apatite-type compounds have been studied by a number of researchers. To improve their properties, it is important to understand the chemical bonding nature, but no study has yet been reported on electron density distribution of apatite-type $Nd_{9.25}Si_6O_{25.88}$. Here, we have determined the crystal structure and electron density distribution by combining a Rietveld method, a maximum-entropy method (MEM) and whole pattern fitting using synchrotron X-ray diffraction intensity measured at room temperature.

Experimental

Synchrotron X-ray powder diffraction data were collected using the multi-detector diffractometer installed at BL-4B$_2$ of Photon Factory, KEK, Tsukuba. The wavelength was determined to be λ=1.206464(1) Å. Diffraction data were collected at 25 °C in the 2θ range from 7° to 154° in the step interval of 0.005° in 2θ. The diffraction data were analyzed by the Rietveld method, RIETAN-FP[1] followed by an application of MEM-based pattern fitting (MPF)[2].

Results and discussion

All the reflections of the diffraction data of the apatite-type $Nd_{9.25}Si_6O_{25.88}$ were indexed by a hexagonal $P6_3/m$ symmetry. The calculated profiles fit well with that of observed one (Fig. 1). The MEM analyses were performed using the structure factors obtained from the Rietveld analysis. The number of structure factors was 587. The MEM calculations were done with the unit cell divided into 100 × 100 × 80 pixels and whole-pattern fitting using RIETAN-FP.[1] Then, the MEM-based pattern fitting was applied which improved the reliability factors. Electron-density image is shown in Fig.2 to visualize the density derived from the MEM calculations. The electron density distribution map (Fig.2) indicates covalent bonding between the Nd2 and O4 atoms, which might be formed by the hybridization of Nd 4f and O 2p electrons. The minimum electron density between the Nd2—O4 bond is 0.60 Å^{-3}. In comparison with the Nd2 atom, Nd1 atom is isolated and more ionic. The electron density among the Nd1 and its neighboring atoms was low, indicating no covalent bonding. It can be seen from the electron density map (Fig.2) that $SiO_{3.98}$ tetrahedrons are hybridized and covalent character of the bond between Si and O is clearly visualized. Each Si atom has covalent bonds with four adjacent oxygen atoms. This covalent bonding is formed by the hybridization of Si 3p and O 2p electrons. The minimum electron density between the Si—O bonds is obtained to be 1.18 Å^{-3}.

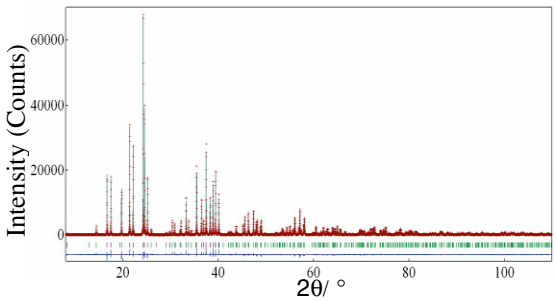

Fig. 1 Rietveld fitting pattern of $Nd_{9.25}Si_6O_{25.88}$ measured at 25°C. Crosses (+) and line denote observed and calculated profile intensities, respectively. Short vertical bars represent Bragg reflection positions. A difference (observed-calculated) plot is shown bellow the profiles.

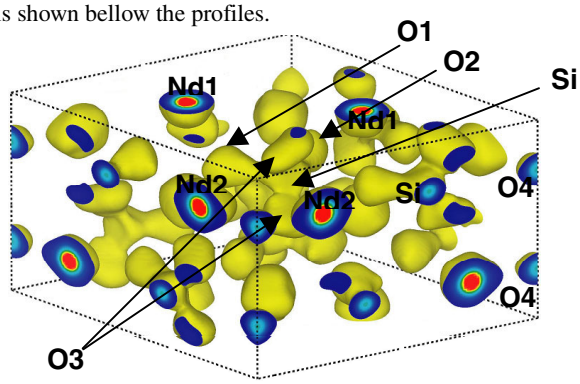

Fig. 2 Equi-electron density surfaces at 1.0 Å^{-3} of apatite-type $Nd_{9.25}Si_6O_{25.88}$ at 25°C.

References

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