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A trial for distinguish of Mn^{3+} and Mn^{4+} ions in $LiMn_2O_4$ by anomalous powder X-ray diffraction with focused beam flat sample method

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Abstract. X-ray diffraction with anomalous scattering (anomalous diffraction) is an effective method to distinguish the positions of atoms which have similar number of electrons in crystal structure. We have been developing a method for anomalous powder X-ray diffraction with synchrotron X-ray by the combination of focused beam, flat sample and area detector and succeeded in the determination of the distribution of cations with neighboring atomic numbers. This method can be applied to analysis of the position of ions with different valence of an atom in crystal structure, therefore we have tried anomalous powder X-ray diffraction experiments of materials that include different valence ions of an atom. $LiMn_2O_4$ was an example of such material. In the crystal structure, a normal spinel, the Mn atoms in octahedral site takes mixed valence state of Mn^{3+} and Mn^{4+}. This material has a phase transition near room temperature and below the phase transition temperature a structure with partial ordering of Mn^{3+} and Mn^{4+} has been proposed. In order to examine anomalous scattering effect of Mn^{3+} and Mn^{4+}, diffraction experiments using X-rays near Mn K edge were conducted. The result of diffraction experiments shows that the diffraction peak intensity change depend on the incident X-ray energy in different manner peak by peak. Powder diffraction data that include anomalous scattering effect can be successfully obtained from material with mixed valence state of Mn^{3+} and Mn^{4+}.

INTRODUCTION

X-ray diffraction with anomalous scattering (anomalous diffraction) is an effective method to distinguish the positions of atoms which have similar number of electrons in crystal structure. Thus, we have been developing a new measurement method for anomalous powder X-ray diffraction with synchrotron X-rays. The method is the combination of focused beam, flat sample and area detectors [1] so we called it focused-beam flat-sample method (FFM). Generally, the combination of flat shape sample and area detector has disadvantage for angular resolution because the large footprint on sample surface makes geometrical peak broadening [2]. However, we found the focusing incident beam in the diffraction plane cancels the geometrical peak broadening and achieves high angular resolution. The FFM can correct the absorption effect without approximation, thus it has an advantage for the anomalous diffraction. We have reported that diffraction peak intensity data obtained by the FFM obviously reflected the anomalous scattering effect [1]. In order to develop the FFM we have constructed apparatuses, a new goniometer for flat shape sample with temperature control system and side loading sample holders. The FFM can be successfully applied for distinguish of atoms with neighboring atomic number. We have applied the FFM to the anomalous diffraction experiment in order to determine Co and Fe site distribution in $CoFe_2O_4$ crystal structure. We obtained powder diffraction data using X-rays near Fe K absorption edge and can successfully determine the Co and Fe site distribution by Rietveld analyses [3].

This method can be applied to analysis of the position of ions with different valence of an atom in crystal structure, therefore we have tried anomalous powder X-ray diffraction experiments of materials that include different valence ions of an atom.

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$LiMn_2O_4$ was an example of such material. The material payed much interest as an anode material of Li ion rechargeable battery, therefore, many material researches have been performed. The material is a normal spinel structure, which octahedral site is occupied by only Mn ions, and the Mn ions takes mix valence state of Mn^{3+} and Mn^{4+}. At ambient temperature $LiMn_2O_4$ takes a cubic structure with the space group $Fd\bar{3}m$(227) and the Mn ions in the octahedral site takes completely disorder state. $LiMn_2O_4$ has a 1st order phase transition just below ambient temperature and the structure of the low temperature phase is an orthorhombic structure with space group Fddd (70) [4]. Ishizawa et al [5] suggested the reason of phase transition is the partial ordering of Mn^{3+} and Mn^{4+} in the octahedral site from the result of single crystal structure analysis, however, the result was conducted only from the size of the octahedral site and no direct observation of Mn^{3+} and Mn^{4+} ions in the crystal structure has not been done yet.

We applied FFM to $LiMn_2O_4$ as a trial experiment of distinguish of ions with different valence of an atom. The results of anomalous diffraction experiment of $LiMn_2O_4$ using X-rays near Mn K absorption edge will be reported. Further, required energy resolution of synchrotron radiation beamline in order to distinguish of ions with different valence will be discussed.

DIFFRACTION EXPERIMENTS

The BL15XU beamline at the Spring-8 was used for powder diffraction experiments [6]. The synchrotron radiation from the planer mode of the undulator were monochromatized by a liquid-nitrogen-cooling Si(111) double-crystal monochromator. An X-ray total reflection double mirror system applied for reduction of higher harmonics.

Diffraction experiments were performed using two wavelength X-rays.

Powder diffraction data without anomalous scattering effects collected using X-rays with the energy of 18.9886keV. A Debye-Scherrer geometry was applied with powder sample stuffed into a capillary with the diameter of 0.1mm. The sample temperature was kept at low temperature phase by a liquid N_2 cooling sample temperature controller. The obtained diffraction data was analysed by the Rietveld method.

Anomalous diffraction experiments carried out using FFM method. The X-rays around Mn K edge energy was used for diffraction experiments. The Mn K-edge energy was determined as 6.5390keV from observation of X-ray absorption profiles of a thin Mn-metal. The 2nd mirror was used for vertical focusing of X-rays. The focal point set at the rotation center of the diffractometer on flat shape samples surface. A side-loading method sample holder developed for FFM, which can insert sample powder from side of sample holder to decrease effect of preferred orientation. The incident X-ray angle to the sample surface was fixed at the angle of θ=7°. Sample temperature was controlled by a sample cooling system with a Peltier device. The focused beam size in vertical direction was estimated as 0.03 mm by slit scanning.

Mythen one-dimensional X-ray detector system used for intensity data collection. The system has been introduced into the high-resolution powder diffractometer at BL15XU in order to increase measurement efficiency [7]. The sample detector distance was designed to be 955mm and the read out pixel size along to the 2θ axis is 0.05mm. The geometry realizes the minimum 2θ step 0.003 degrees.

Powder of $LiMn_2O_4$ without any dopant synthesized by solid phase reaction method was used for diffraction experiment.

The Mn K edge energy was determined by absorption observation with a Mn metal thin foil. X-rays with the energy of little bit higher and lower of the K edge were applied for diffraction experiments. The difference of the K edge energy of ions with different valence of an atom is few eV. As the energy resolution of BL15XU optics is estimated to be 1 eV around Mn K edge energy, it can be applied to the present experiment. Powder diffraction data from low temperature phase of $LiMn_2O_4$ were collected and used for analysis.

RESULTS AND DICUSSION

Figure 1 shows that the result of the Rietveld analysis of low temperature phase of $LiMn_2O_4$ using X-rays with the energy of 18.9886keV. A crystal structure model with space group Fddd (70) [4] gave proper fitting results. The final reliable factors Rp, Rwp, Rb and Rf(%) were 4.24, 6.27, 9.13 and 12.70, respectively. The Rb and Rf values were worse compare to the Rp and Rwp.

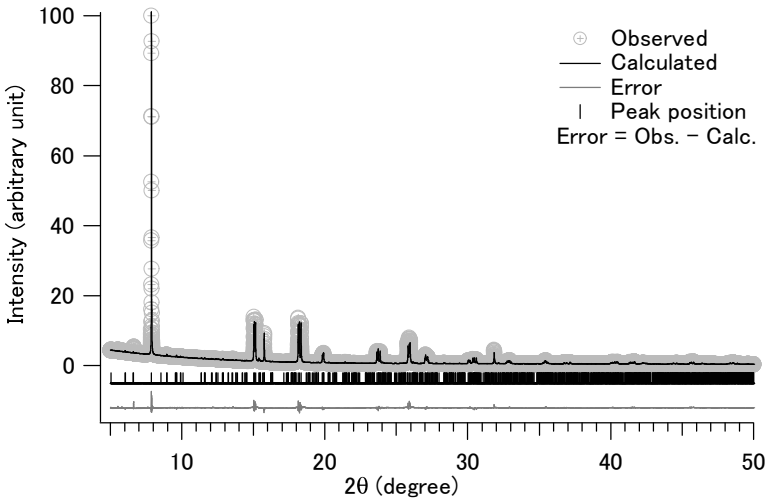

FIGURE 1. Result of Rietveld analysis of $LiMn_2O_4$ low temperature phase with space group Fddd (70) using diffraction intensity data without anomalous scattering effects obtained X-rays with the energy of 18.9886keV.

Figure 2 shows the peak profile change depends on the incident X-ray energy around Mn K absorption edge. The energy value in the figure presents deviation from that of Mn metal K edge. The K edge of Mn^{3+} ions supposed to be around +2.5eV higher point and that of Mn^{4+} is a little higher than Mn^{3+}. The significant difference of the atomic scattering factors including anomalous scattering effect appear only in the narrow region near Mn^{3+} and Mn^{4+} K edges.

Diffraction intensity change according to the X-ray energy means of Mn^{3+} and Mn^{4+} ordering structure. If Mn^{3+} and Mn^{4+} takes random distribution in Mn site, the anomalous scattering factor is the average of Mn^{3+} and Mn^{4+} including the anomalous scattering effect. In this case diffraction intensity change depending on incident X-ray energy cannot be observed.

In Fig.2 a small but obvious peak appeared at around 53.5 degrees, according to the X-ray energy increase. The incident energy region where the peak is observed corresponds to the region higher than Mn^{3+} K edge. The peak occurred from a super-structure that made by Mn^{3+} and Mn^{4+} with different atomic scattering factors that is caused by the difference of anomalous scattering factors, f' and f". Three peaks in the 2θ range of 54.3 to 55.3 are the result of splitting of 4 0 0 reflection of cubic structure of ambient temperature phase. These peaks in order from lower 2θ corresponds to 0 12 0, 12 0 0 and 0 0 4 of orthorhombic low temperature phase with space group of Fddd(70). The 0 0 4 peak intensity monotonically decreases according to the increase of incident X-ray energy. The 0 0 4 peak intensity includes information for the c axis of the orthorhombic structure and the intensity change suggests existence of any order structure of Mn^{3+} and Mn^{4+} along the c axis. We can obtain diffraction data including structural information of Mn^{3+} and Mn^{4+} ordering properly by this anomalous diffraction experiment.

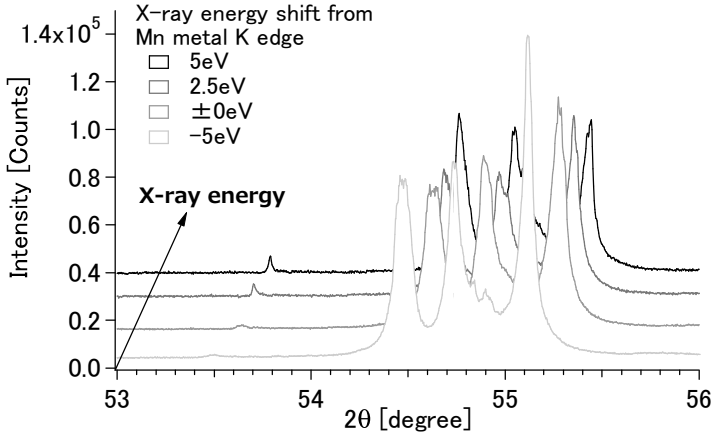

FIGURE 2. X-ray energy dependence of powder diffraction intensities of low temperature phase of $LiMn_2O_4$ with X-rays near the Mn K absorption edge.

Figure 3. shows the calculated energy resolution of monochrometer of BL15XU based on beamline parameters. The solid line shows the ΔE value of Si(111) and around Mn K edge energy the value is about 1.33 keV. The difference of Mn K absorption edge energy between Mn^{3+} and Mn^{4+} is estimated a few eV considering the chemical shift observed by X-ray absorption pattern and shape of the curve of anomalous scattering factors. The X-ray energy resolution was just barely applicable for the anomalous diffraction experiments to distinguish Mn ions even if a 3rd generation undulator beamline was used.

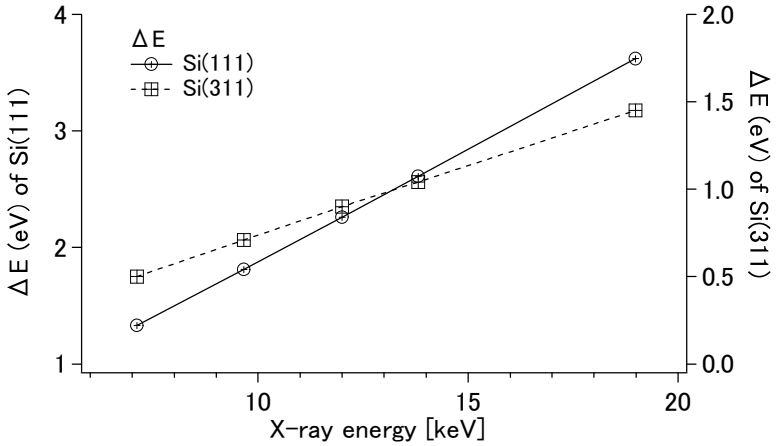

FIGURE 3. X-ray energy resolution of monochromator of BL15XU beamline of SPring-8

On the other hand the broken line shows the ΔE value of Si(311) and the values are better than that of Si(111). The use of higher diffraction plane than Si(111) of monochromator is essential for anomalous diffraction experiments.

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