

Local Structure in Pyrochlore Niobates

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The spin frustration in the pyrochlore oxides, which have the chemical formula of $A_2B_2O_7$, provides interesting phenomena such as the spin ice state, where the two-in-two-out spin configuration is produced in the tetrahedra of the A site. If it is possible that the occupation of the electron (hole) in the B site in the pyrochlore structure corresponds to the out (in) state of the spin, one can expect the “charge ice” state as the analogy of the spin ice. If this local charge order is also coupled with the lattice distortion, the local dipole moment is anticipated to be formed in the Nb tetrahedra. For the realization of the charge ice state, the average valence of the transition-metal ion has to be a half integer in the pyrochlore oxides. Istomin *et al.* synthesized the pyrochlore niobates $YCaNb_2O_7$ and $NdCaNb_2O_7$ [1], in which the Nb valence is +4.5. Recently, Cava *et al.* also reported the neutron diffraction in $YCaNb_2O_7$ and performed its structure analysis [2].

The pyrochlore niobates $YCaNb_2O_7$ and $NdCaNb_2O_7$ are synthesized by use of the floating zone furnace. In these compounds, we find the Debye relaxation of the dielectric constants suggesting the ferroelectric state. It is essential to investigate the Nb charge and its position, in order to investigate the mechanism of the dielectric properties. We measured the X-ray absorption spectra (XAS) in SPring-8(BL14B1). The Nb K edge energy depends on the average charge of the Nb ion. The Nb charge in $YCaNb_2O_7$ and $NdCaNb_2O_7$ is estimated to be about 4.5 by the energy position of the K edge. This XAS result is in agreement with the Nb charge estimated by the thermobalance method. Figure 1 shows the Fourier transform of the EXAFS (extended X-ray absorption fine structure) function. The peak around $r=1.5\text{ \AA}$ corresponds to the nearest oxygen from the Nb ion, while the peak around $r=3.3\text{ \AA}$ to the nearest neighbor Nb ion and the Y, Nd and Ca ions in the A -site. In the pyrochlore oxides, the B -site ion is located in the center of the oxygen octahedron. The oxygen sites around the Nb ion are equivalent in ideal pyrochlore structure. The height of the peak around $r=1.5\text{ \AA}$ is reduced in $YCaNb_2O_7$ and $NdCaNb_2O_7$, as compared to $Cd_2Nb_2O_7$, which has the ideal pyrochlore structure at the room temperature. Thus, the Fourier transform of the EXAFS function reveals that the nearest oxygen sites are not equivalent in $YCaNb_2O_7$ and $NdCaNb_2O_7$. Cava *et al.* reported that the Nb ion is displaced either towards or away from the centers of the B -site tetrahedra [2]. Assuming this type of the Nb displacement, we calculated the EXAFS function in the cluster containing the Nd, Y, Ca, Nb and O ions around the Nb ion. Here, we consider the case of the two Nb displacements (the two-in or two-out configuration) or the four Nb displacements (the two-in-two-out configuration) of the B -site tetrahedra. In the two-in-two-out configuration, it is difficult to reproduce the structure of the two peaks around $r=3\text{ \AA}$, since the Nb-Nb distance is not sensitive to the Nb displacement. This analysis around the peaks near $r=1.5\text{ \AA}$ and $r=3.3\text{ \AA}$ indicate the Nb displacements of about $0.041\text{ \AA}\sim 0.103\text{ \AA}$, which is in agreement with the result of the neutron diffraction [2]. I will discuss the origin of the ferroelectric state and the Nb displacement in the pyrochlore niobates.

[1] S.Y.Istomin *et al.*, *Mater. Res. Bull.* **32**, 421 (1997).

[2] T.M.McQueen *et al.*, *J. Phys: Condens. Matter* **20**, 235210 (2008).

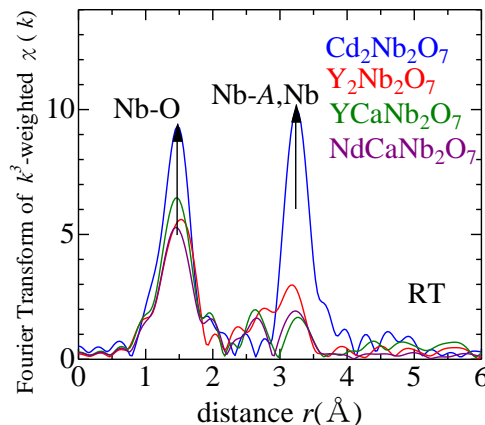


Fig.1 : The Fourier transform of the EXAFS function in the pyrochlore Niobates