Comparison of Charge Distribution in KNb_2PS_{10} and Nb_2PS_{10} by Solid State ^{31}P MAS NMR

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Solid state ^{31}P magic angle spinning (MAS) nuclear magnetic resonance (NMR) data of metal thiophosphates, Nb_2PS_{10} and KNb_2PS_{10} are employed to identify electron density differences between the compounds. The X-ray diffraction results of the compounds were reported in previous publications: reference 1 for Nb_2PS_{10} and reference 2 for KNb_2PS_{10}. Nb_2PS_{10} is a thiophosphate composed of infinite two-dimensional planes. The plane consists of infinite chains of NbS_8 bicapped trigonal prisms sharing a rectangular face and PS_4 polyhedra linking the chains one side to another. There is no strong bonds between the planes except van der Waals' force. KNb_2PS_{10} has a common structure with Nb_2PS_{10} of NbS_8 bicapped trigonal prisms sharing a rectangular face and PS_4 polyhedra. But K ions are located between the planes in KNb_2PS_{10}. Another difference between Nb_2PS_{10} and KNb_2PS_{10} is that PS_4 polyhedra in KNb_2PS_{10} are oriented in the same direction and do not link NbS_8 chains. Thus, KNb_2PS_{10} consists of infinite one-dimensional chains of NbS_8 and PS_4 units rather than two-dimensional planes. Addition of K to Nb_2PS_{10} compound is expected to bring electronic charge distribution changes as well as structural changes. There is a report that d- block orbitals of the highly oxidized metals are responsible for Li intercalation to the M_2PS_{10} (M=V, Nb) compounds rather than the P-S or S-S antibonding.[4] Chemical shift parameters are sensitive to electronic and structural differences, therefore, we employed ^{31}P NMR to compare electron density around phosphorous in Nb_2PS_{10} and KNb_2PS_{10}. Although K in KNb_2PS_{10} is not incorporated electrochemically, the overall electronic differences between Nb_2PS_{10} and KNb_2PS_{10} can give us a clue where the electron density increases on alkali atom incorporation into the compounds.

Preparation procedures were described in detail in previous reports.[1,2] KNb_2PS_{10} and Nb_2PS_{10} are prepared by the reaction of the elements Nb, P, and S with an elemental ratio of 2 : 1 : 10 for Nb : P : S in the presence of and in the absence of the eutectic mixture of KCl/LiCl, respectively.

All experiments are carried out with the UNITYplus NMR system (Varian Associates Inc., U. S. A.) of 7.05 Tesla. MAS rate between 1.4, and 4.2 kHz, and 2 μs pulse length corresponding to 23° flip angle are employed. Samples are ground to fine powders before NMR experiments. Chemical shift is referenced to the external 85% H_3PO_4 aqueous solution and the reading error of center peak chemical shift (δ_{obs}) is within

1 ppm. The ^{31}P MAS spectra are simulated with a home-made simulation program to obtain principal values of the chemical shielding tensor (δ_{11}, δ_{22}, and δ_{33}). Isotropic chemical shift (δ_i), asymmetry parameter (η), and chemical shift anisotropy ($\Delta\delta$) are derived from δ_{11}, δ_{22}, and δ_{33} values using the following equations.[3]

$$\delta_i = (1/3)(\delta_{11} + \delta_{22} - \delta_{33})$$

for $|\delta_{11} - \delta_i| \geq |\delta_{33} - \delta_i|$,

$$\Delta\delta = (3/2)(\delta_{11} - \delta_i), \eta = (\delta_{22} - \delta_{33})/(\delta_{11} - \delta_i)$$

for $|\delta_{11} - \delta_i| |\delta_{33} - \delta_i|$,

$$\Delta\delta = (3/2)(\delta_{33} - \delta_i), \eta = (\delta_{22} - \delta_{11})/(\delta_{33} - \delta_i).$$

Representative ^{31}P MAS spectra of Nb_2PS_{10} and KNb_2PS_{10} samples and spectrum simulation are shown in Figure 1. Chemical shift parameters from the spectrum simulation of the ^{31}P MAS spectra obtained at various rotation rates are summarized in Table 1. Previous studies have indicated that ^{31}P chemical shift is mainly influenced by three factors: (1) the number and electronegativity of the nearest-neighbor ligands, (2) the occupation of the π bonding orbitals on the phosphorous atom, and (3) the bond angles about the phosphorous atom.[5,6] For orthophosphate ions, a good correlation between $|\Delta\delta|$ and the average deviation of the O-P-O bond angle from that of a perfect tetrahedron (109°28') was obtained.[7] Also δ_i of an orthophosphate ion was well correlated with the average P-O bond length.[7] The latter correlation can be understood from the observation that the average P-O bond length decreases as the number of electrons in π orbitals increases[7,8] while δ_i decreases with increasing number of electrons in π bonding orbitals for the orthophosphate ions.[5,8] For our Nb_2PS_{10} and KNb_2PS_{10} samples, factor (1) is expected to be constant, or nearly so, thus can be ignored. We may apply the same methods used for orthophosphate ions to PS_4 units in our samples considering the fact that oxygen and sulfur belong to the same group 16 in the periodic table. Then, the smaller δ_i and the greater $|\Delta\delta|$ of KNb_2PS_{10} than those of Nb_2PS_{10} can be explained in terms of the shorter average P-S bond length and the bigger average deviation of S-P-S bond angle from 109°28' of KNb_2PS_{10}. The average bond length of four P-S bonds is 2.044 ± 0.005 and 2.036 ± 0.005 Å for Nb_2PS_{10} and KNb_2PS_{10}, respectively. The average deviation of S-P-S bond angle from ideal tetrahedron was 3.5 ± 0.2 and 4.6 ± 0.2° for Nb_2PS_{10} and KNb_2PS_{10}, respectively.

In our previous studies, the incorporation of alkali metals into the Nb_2PS_{10} host structure by electrochemical processes

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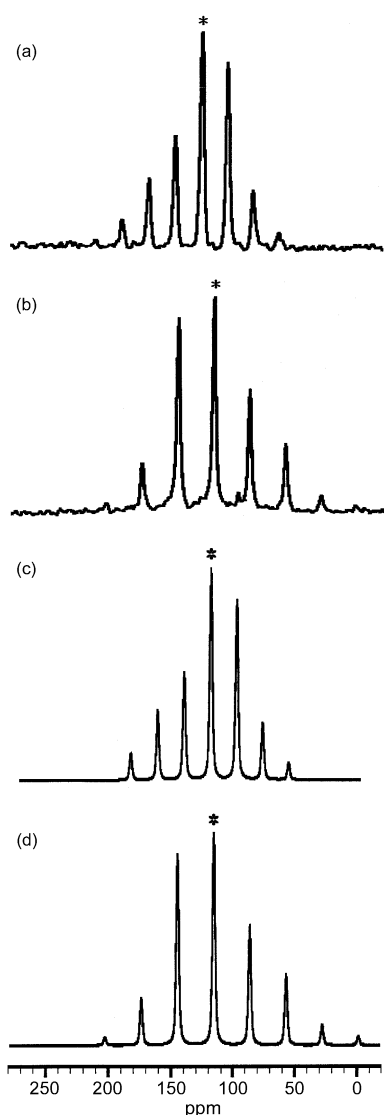
Figure 1. ^{31}P MAS NMR spectra of (a) Nb$_2$PS$_{10}$ at 2.57 kHz spinning rate and (b) KNb$_2$PS$_{10}$ at 3.50 kHz spinning rate. Simulated ^{31}P MAS NMR spectra (c) with parameters of 2.57 kHz spinning rate, 121.49 MHz Larmor frequency. δ_{11} = 182.0 ppm. δ_{22} = 118.0 ppm. δ_{33} = 77.0 ppm. and 400Hz line broadening and (d) with parameters of 3.50 kHz spinning rate. 121.49 MHz Larmor frequency. δ_{11} = 177.5 ppm. δ_{22} = 133.5 ppm. δ_{33} = 39.5 ppm. and 400Hz line broadening. Center peaks are marked by *.

failed. Thus, it is still a question which part of the host compound plays a role as an electron acceptor for alkali metal intercalation. However, our NMR results can be taken as an evidence that electron density around P increases on average as K is added to the Nb$_2$PS$_{10}$ because smaller δ_i value of KNb$_2$PS$_{10}$ indicates greater number of electrons in π orbitals of P in KNb$_2$PS$_{10}$ than in Nb$_2$PS$_{10}$. Among all the P-S bonds, contribution to this increased average electron density around P is expected to be more from the P-S bond with a terminal S in KNb$_2$PS$_{10}$. The length difference between this and the corresponding P-S bond in Nb$_2$PS$_{10}$ is 0.14 Å which is biggest among all P-S bond length differences between the KNb$_2$PS$_{10}$ and Nb$_2$PS$_{10}$. Therefore, we can conclude that the presence of K in KNb$_2$PS$_{10}$ results in the increase of electron density

Table 1. ^{31}P chemical shift anisotropy parameters of compounds

Compound	δ_{11} (ppm)	δ_{22} (ppm)	δ_{33} (ppm)	δ_i (ppm)	η	$|\Delta\delta|$ (ppm)	δ_{obs}* (ppm)
KNb$_2$PS$_{10}$	177.5	133.5	39.5	116.8	0.57	116.0	117
Nb$_2$PS$_{10}$	182.0	118.0	77.0	125.7	0.73	84.5	126

*Experimentally observed chemical shift.

around P-S bonds, especially the ones with terminal S. This does not necessarily mean that the axis of δ_{33} coincides with those of the P-S bonds with terminal S even though it is more likely in terms of symmetry. The orientation of δ_{33} axis can be determined only with single crystal samples, however, the KNb$_2$PS$_{10}$ and Nb$_2$PS$_{10}$ single crystals big enough for NMR experiments have not been able to be grown. Although we cannot completely exclude the possibility that d- block orbitals of Nb behave as an acceptor for *some* of electrons from K, our results clearly indicate that phosphorous and sulfur are principal electron acceptors, especially by P-S bonds with terminal S in KNb$_2$PS$_{10}$.

In summary, electron density around P in KNb$_2$PS$_{10}$ and Nb$_2$PS$_{10}$ is studied by comparison of the ^{31}P MAS NMR spectra of the compounds. Isotropic chemical shift and chemical shift anisotropy of KNb$_2$PS$_{10}$ are smaller and wider than those of Nb$_2$PS$_{10}$, respectively. The smaller isotropic chemical shift is correlated with the shorter average P-S bond length of PS$_4$ unit and the wider chemical shift anisotropy is due to the wider average deviation of S-P-S bond angle of PS$_4$ unit from 109.5°. The shorter average P-S bond length can be interpreted as more electrons in π bonding orbitals of the P-S bond. Our results imply that electrons from K (electron donner) mainly go to phosphorous and sulfur rather than to the d-orbitals of Nb.

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