

## Comparison of Charge Distribution in KNb<sub>2</sub>PS<sub>10</sub> and Nb<sub>2</sub>PS<sub>10</sub> by Solid State <sup>31</sup>P MAS NMR

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Solid state <sup>31</sup>P magic angle spinning (MAS) nuclear magnetic resonance (NMR) data of metal thiophosphates, Nb<sub>2</sub>PS<sub>10</sub> and KNb<sub>2</sub>PS<sub>10</sub> 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<sub>2</sub>PS<sub>10</sub> and reference 2 for KNb<sub>2</sub>PS<sub>10</sub>. Nb<sub>2</sub>PS<sub>10</sub> is a thiophosphate composed of infinite two-dimensional planes. The plane consists of infinite chains of NbS<sub>8</sub> bicapped trigonal prisms sharing a rectangular face and PS<sub>4</sub> polyhedra linking the chains one side to another. There is no strong bonds between the planes except van der Waals' force. KNb<sub>2</sub>PS<sub>10</sub> has a common structure with Nb<sub>2</sub>PS<sub>10</sub> of NbS<sub>8</sub> bicapped trigonal prisms sharing a rectangular face and PS<sub>4</sub> polyhedra. But K<sup>+</sup> ions are located between the planes in KNb<sub>2</sub>PS<sub>10</sub>. Another difference between Nb<sub>2</sub>PS<sub>10</sub> and KNb<sub>2</sub>PS<sub>10</sub> is that PS<sub>4</sub> polyhedra in KNb<sub>2</sub>PS<sub>10</sub> are oriented in the same direction and do not link NbS<sub>8</sub> chains. Thus, KNb<sub>2</sub>PS<sub>10</sub> consists of infinite one-dimensional chains of NbS<sub>8</sub> and PS<sub>4</sub> units rather than two-dimensional planes. Addition of K to Nb<sub>2</sub>PS<sub>10</sub> 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<sub>2</sub>PS<sub>10</sub> (M=V, Nb) compounds rather than the P-S or S-S antibonding.<sup>4</sup> Chemical shift parameters are sensitive to electronic and structural differences, therefore, we employed <sup>31</sup>P NMR to compare electron density around phosphorous in Nb<sub>2</sub>PS<sub>10</sub> and KNb<sub>2</sub>PS<sub>10</sub>. Although K in KNb<sub>2</sub>PS<sub>10</sub> is not incorporated electrochemically, the overall electronic differences between Nb<sub>2</sub>PS<sub>10</sub> and KNb<sub>2</sub>PS<sub>10</sub> 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.<sup>1,2</sup> KNb<sub>2</sub>PS<sub>10</sub> and Nb<sub>2</sub>PS<sub>10</sub> 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<sub>3</sub>PO<sub>4</sub> aqueous solution and the reading error of center peak chemical shift ( $\delta_{\text{obs}}$ ) is within

1 ppm. The <sup>31</sup>P MAS spectra are simulated with a home-made simulation program to obtain principal values of the chemical shielding tensor ( $\delta_{11}$ ,  $\delta_{22}$ , and  $\delta_{33}$ ). Isotropic chemical shift ( $\delta_i$ ), asymmetry parameter ( $\eta$ ), and chemical shift anisotropy ( $\Delta\delta$ ) are derived from  $\delta_{11}$ ,  $\delta_{22}$ , and  $\delta_{33}$  values using the following equations,<sup>3</sup>

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

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

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

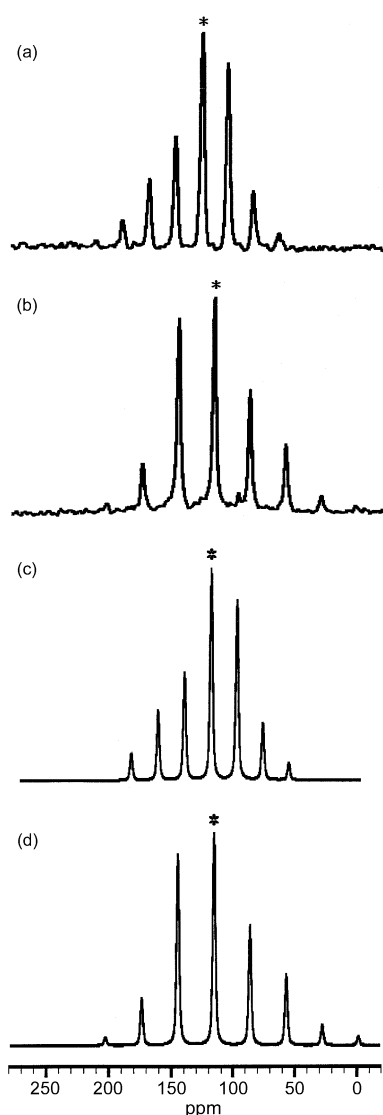
for  $|\delta_{11} - \delta_i| < |\delta_{33} - \delta_i|$ ,

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

Representative <sup>31</sup>P MAS spectra of Nb<sub>2</sub>PS<sub>10</sub> and KNb<sub>2</sub>PS<sub>10</sub> samples and spectrum simulation are shown in Figure 1. Chemical shift parameters from the spectrum simulation of the <sup>31</sup>P MAS spectra obtained at various rotation rates are summarized in Table 1. Previous studies have indicated that <sup>31</sup>P chemical shift is mainly influenced by three factors: (1) the number and electronegativity of the nearest-neighbor ligands, (2) the occupation of the  $\pi$  bonding orbitals on the phosphorous atom, and (3) the bond angles about the phosphorous atom.<sup>5,6</sup> 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.<sup>7</sup> Also  $\delta_i$  of an orthophosphate ion was well correlated with the average P-O bond length.<sup>7</sup> The latter correlation can be understood from the observation that the average P-O bond length decreases as the number of electrons in  $\pi$  orbitals increases<sup>7,8</sup> while  $\delta_i$  decreases with increasing number of electrons in  $\pi$  bonding orbitals for the orthophosphate ions.<sup>5,8</sup> For our Nb<sub>2</sub>PS<sub>10</sub> and KNb<sub>2</sub>PS<sub>10</sub> 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<sub>4</sub> units in our samples considering the fact that oxygen and sulfur belong to the same group 16 in the periodic table. Then, the smaller  $\delta_i$  and the greater  $|\Delta\delta|$  of KNb<sub>2</sub>PS<sub>10</sub> than those of Nb<sub>2</sub>PS<sub>10</sub> 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<sub>2</sub>PS<sub>10</sub>. The average bond length of four P-S bonds is 2.044 ± 0.005 and 2.036 ± 0.005 Å for Nb<sub>2</sub>PS<sub>10</sub> and KNb<sub>2</sub>PS<sub>10</sub>, 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<sub>2</sub>PS<sub>10</sub> and KNb<sub>2</sub>PS<sub>10</sub>, respectively.

In our previous studies, the incorporation of alkali metals into the Nb<sub>2</sub>PS<sub>10</sub> host structure by electrochemical processes

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**Figure 1.**  $^{31}\text{P}$  MAS NMR spectra of (a)  $\text{Nb}_2\text{PS}_{10}$  at 2.57 kHz spinning rate and (b)  $\text{KNb}_2\text{PS}_{10}$  at 3.50 kHz spinning rate. Simulated  $^{31}\text{P}$  MAS NMR spectra (c) with parameters of 2.57 kHz spinning rate, 121.49 MHz Larmor frequency,  $\delta_{11} = 182.0$  ppm,  $\delta_{22} = 118.0$  ppm,  $\delta_{33} = 77.0$  ppm, and 400Hz line broadening and (d) with parameters of 3.50 kHz spinning rate, 121.49 MHz Larmor frequency,  $\delta_{11} = 177.5$  ppm,  $\delta_{22} = 133.5$  ppm,  $\delta_{33} = 39.5$  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  $\text{Nb}_2\text{PS}_{10}$  because smaller  $\delta_i$  value of  $\text{KNb}_2\text{PS}_{10}$  indicates greater number of electrons in  $\pi$  orbitals of P in  $\text{KNb}_2\text{PS}_{10}$  than in  $\text{Nb}_2\text{PS}_{10}$ . 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  $\text{KNb}_2\text{PS}_{10}$ . The length difference between this and the corresponding P-S bond in  $\text{Nb}_2\text{PS}_{10}$  is 0.14 Å which is biggest among all P-S bond length differences between the  $\text{KNb}_2\text{PS}_{10}$  and  $\text{Nb}_2\text{PS}_{10}$ . Therefore, we can conclude that the presence of K in  $\text{KNb}_2\text{PS}_{10}$  results in the increase of electron density

**Table 1.**  $^{31}\text{P}$  chemical shift anisotropy parameters of compounds

Compound	$\delta_{11}$ (ppm)	$\delta_{22}$ (ppm)	$\delta_{33}$ (ppm)	$\delta_i$ (ppm)	$\eta$	$ \Delta\delta $ (ppm)	$\delta_{\text{obs}}^*$ (ppm)
$\text{KNb}_2\text{PS}_{10}$	177.5	133.5	39.5	116.8	0.57	116.0	117
$\text{Nb}_2\text{PS}_{10}$	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  $\delta_{33}$  coincides with those of the P-S bonds with terminal S even though it is more likely in terms of symmetry. The orientation of  $\delta_{33}$  axis can be determined only with single crystal samples, however, the  $\text{KNb}_2\text{PS}_{10}$  and  $\text{Nb}_2\text{PS}_{10}$  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  $\text{KNb}_2\text{PS}_{10}$ .

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

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## References

- Brec, R.; Grenouilleau, P.; Evain, M.; Rouxel, J. *Rev. Chim. Min.* **1983**, *20*, 295.
- Do, J.; Yun, H. *Inorg. Chem.* **1996**, *35*, 3729.
- Duncan, T. M. *A Compilation of Chemical Shift Anisotropies*; The Farragut Press: Chicago, 1990; p 3.
- Evain, M.; Brec, R.; Whangbo, M.-H. *J. Solid State Chem.* **1987**, *71*, 244.
- Topics in Phosphorous Chemistry*; Crutchfield, M. M., Dungan, C. H., Van Wazer, J. R., Eds.; Interscience: New York, 1967; Vol. 5, Chap. 3.
- Techniques of Chemistry*; Bentley, K. W., Kirby, G. W., Eds.; Wiley-Interscience: New York, 1972; Vol. 4, p 355.
- Turner, G. L.; Smith, K. A.; Kirkpatrick, R. J.; Oldfield, E. *J. Magn. Res.* **1986**, *70*, 408.
- Andrew, E. R.; Bryant, D. J.; Cashell, E. M.; Dunell, B. A. *Chem. Phys. Lett.* **1981**, *77*, 614.