CHEMISTRY LETTERS, pp. 893-896, 1993.

Structural Study of $ZnZr_4(PO_4)_6$ Solid Electrolyte

Katsuhiro NOMURA,* Shoichiro IKEDA, Hideki MASUDA, and Hisahiko EINAGA
Department of Applied Chemistry, Faculty of Engineering,
Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466

The crystal structure of $ZnZr_4(PO_4)_6$, a member of β-$Fe_2(SO_4)_3$-type solid electrolyte, has been determined by X-ray diffraction method. There are two disordered zinc ions in zirconium phosphate framework, which are characterized by distorted polyhedra of $Zn(1)O_5$ and $Zn(2)O_5$ with the occupation ratio of about 2 : 1. The ionic conduction behavior of this solid electrolyte is compared with that of NASICON-type one.

In the last few decades, many kinds of β-$Fe_2(SO_4)_3$-type compounds have been investigated,[1-3] some of which show relatively high ionic conductivity by the location of interstitial (mobile) cations.[2,3] These mobile cations have mostly been focused on Li^+ ion;[2] divalent cations, e.g. Mg^{2+}, Zn^{2+}, etc.,[3] are rarely paid attention to. In our research on a series of zirconium phosphate solid electrolytes, $MZr_2(PO_4)_3$ ($M = M^+$ (M^IZP), or 0.5 M^{2+} ($M^{II}ZP$)), we have found that the Li, Mg, Mn, Co, Ni, and Zn compounds crystallize in the β-$Fe_2(SO_4)_3$-type structure.[3,4] Ionic radii of these mobile cations were all smaller than 0.97 Å.[5] Furthermore, their ionic conductivities were less dependent on the size of the mobile cation as compared with those of NASICON-type compounds for $M^{II}ZP$. In the present study, we made the single-crystal X-ray structure analysis of $ZnZr_4(PO_4)_6$ (ZnZP) solid electrolyte in order to elucidate this unique conduction behavior of $M^{II}ZP$ with β-$Fe_2(SO_4)_3$-type structure.

Single crystals suitable for X-ray diffraction measurement were prepared in the following way:[6] A homogeneous mixture of ZnO (0.488 g, reagent grade), ZrO_2 (2.464 g, 99.9%), P_2O_5 (2.129 g, reagent grade), and B_2O_3 (4.176 g, reagent grade) was placed in a platinum crucible (25 ml), was heated to 1200 °C at the rate of 20 °C min^{-1}, and then was kept at this temperature for 24 h. The reaction mixture was subsequently cooled to 800 °C at the rate of 3 °C h^{-1} and was allowed to stand to room temperature. The crystals were isolated from the solid mass by dissolving the soluble substances in boiling water and then washing the residue with a hot diluted HCl solution.

A colorless, transparent crystal (0.1 x 0.1 x 0.1 mm^3) was chosen for the single crystal structure study. Diffraction intensities were measured using an Enraf-Nonius CAD-4 automated four-circle diffractometer with graphite-monochromatized Mo-Kα radiation (λ

= 0.71073 Å) at 23 °C. The unit-cell parameters were determined from the setting angles (20° ≦ 2θ ≦ 30°) of 25 reflections. Based on the systematic absences of $h0l$ for $h+l = 2n + 1$ and $0k0$ for $k = 2n + 1$, the space group was determined to be $P2_1/n$. Crystal data: $Zn_{0.5}Zr_2(PO_4)_3$, F.W. = 1000.88, monoclinic, a = 8.8435(2), b = 8.9598(1), c = 12.3974(2) Å , β = 90.310(2)°, V = 982.13 Å ^{3}, Z = 4, D_X = 3.384 g cm^{-3}. All the reflections were corrected for Lorentz and polarization effects. The data were corrected for absorption firstly by using psi-scan profiles and subsequently by the application of the DIFABS procedure.[7)] Based on 952 unique reflections with $|I_0| > 3\sigma(I_0)$, the structure was solved by the heavy-atom method and the subsequent Fourier procedure and refined by the full-matrix least-squares method assuming anisotropic thermal parameters to R = 0.092.

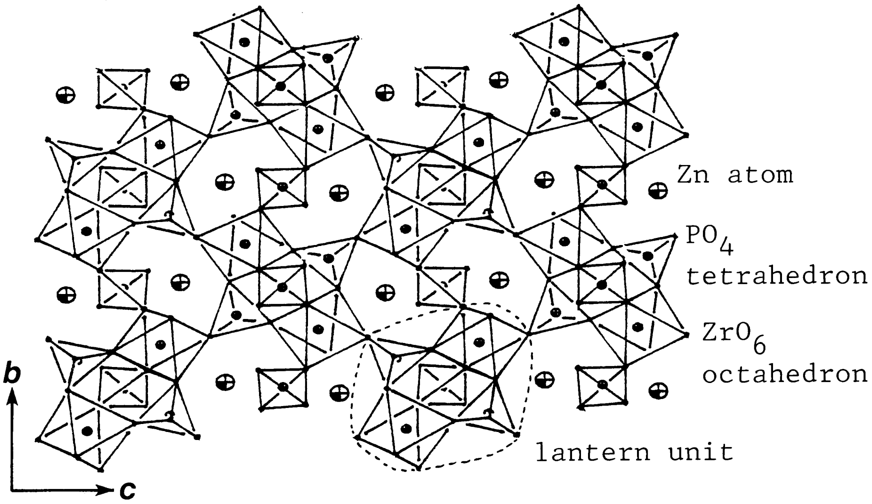

Fig. 1. The ORTEP drawing of $ZnZr_4(PO_4)_6$ viewed along a-axis (β-$Fe_2(SO_4)_3$-type structure). The partly filled circles are zinc atoms.

Table 1. Interatomic distances (Å) and angles (degree) around zinc atoms

Type	Value	Type	Value
Zn(1)-O(1)	2.20(3)	Zn(2)-O(3)	2.30(4)
Zn(1)-O(5)	2.08(3)	Zn(2)-O(6)	2.07(4)
Zn(1)-O(5a)	2.97(3)	Zn(2)-O(9)	2.89(4)
Zn(1)-O(8)	2.25(3)	Zn(2)-O(9a)	2.17(4)
Zn(1)-O(11)	2.15(3)	Zn(2)-O(12)	2.24(3)
O(1)-Zn(1)-O(5)	143.(1)	O(3)-Zn(2)-O(6)	84.(1)
O(1)-Zn(1)-O(5a)	62.6(1)	O(3)-Zn(2)-O(9)	66.(1)
O(1)-Zn(1)-O(8)	97.(1)	O(3)-Zn(2)-O(9a)	137.(2)
O(1)-Zn(1)-O(11)	81.(1)	O(3)-Zn(2)-O(12)	97.(1)
O(5)-Zn(1)-O(5a)	136.5(9)	O(6)-Zn(2)-O(9)	69.(1)
O(5)-Zn(1)-O(8)	82.(1)	O(6)-Zn(2)-O(9a)	135.(2)
O(5)-Zn(1)-O(11)	134.(1)	O(6)-Zn(2)-O(12)	118.(2)
O(5a)-Zn(1)-O(8)	56.(1)	O(9)-Zn(2)-O(9a)	137.(1)
O(5a)-Zn(1)-O(11)	63.9(9)	O(9)-Zn(2)-O(12)	57.(1)
O(8)-Zn(1)-O(11)	112.(1)	O(9a)-Zn(2)-O(1)	81.(1)

As shown in Fig. 1, the X-ray structure analysis has revealed that the zirconium phosphate framework $(Zr_2P_3O_{12})^-$ consists of corner-linked ZrO_6 octahedra and PO_4 tetrahedra in such a way that each oxygen atom bonds to one Zr atom and one P atom, i.e., each ZrO_6 octahedron is connected to six PO_4 tetrahedra, while each PO_4 tetrahedron is linked to four ZrO_6 octahedra. The basic unit is constituted of two

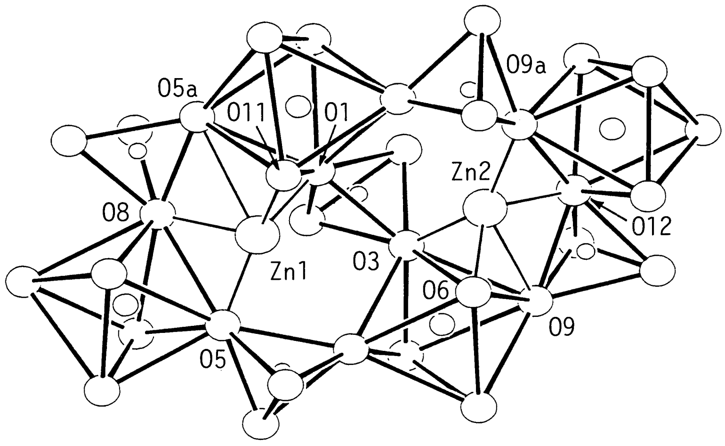

Fig. 2. The ORTEP drawing around $Zn(1)O_5$ and $Zn(2)O_5$ polyhedra (β-$Fe_2(SO_4)_3$-type structure).

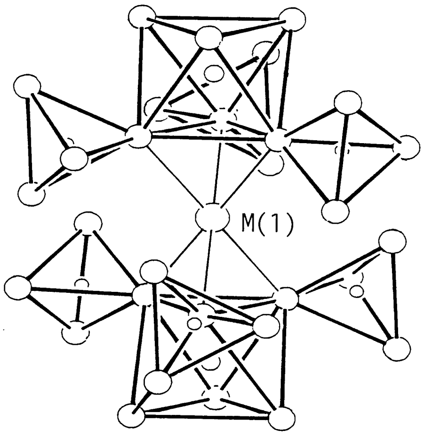

Fig. 3. The ORTEP drawing around M(1)-site in MZP with NASICON-type structure.[9]

ZrO_6 octahedra joined with three PO_4 tetrahedra; these $Zr_2P_3O_{18}$ (lantern) unit is linked with adjacent units via the vertices in such a fashion that the *a-b* layers including their units are related to each other by a crystallographical screw axis (Fig. 1).

Interestingly, the interstitial Zn^{2+} ions were found in two greatly distorted polyhedra, $Zn(1)O_5$ and $Zn(2)O_5$ (Fig. 2), in which the two zinc positions are disordered. The interatomic distances and angles around these Zn atoms are listed in Table 1. The Zn-O distances range from 2.08 to 2.97 Å and 2.07 to 2.89 Å for Zn(1) and Zn(2), respectively (four Zn-O distances are short and one Zn-O distance long for both cases); they are all longer than the sum of tetrahedrally coordinated Shannon crystal radii, i.e., 1.98 Å.[4] These data indicate that the Zn(1) and Zn(2) cations are less tightly bound to the zirconium phosphate framework and may therefore be related to a high conductivity.

The occupations of these two zinc sites were refined to 0.37 and 0.15 for Zn(1) and Zn(2), respectively. This fractional occupation means that the interstitial Zn^{2+} ions are randomly located over these Zn(1) and Zn(2) sites. This "average structure" can contribute to the high ionic conductivity of ZnZP.[8]

In ZnZP with β-$Fe_2(SO_4)_3$-type structure, the Zn^{2+} ions are loosely bonded to framework oxygens as mentioned above. The bottle-neck of the conduction pathway is expected to be near the center of a triangle formed by three oxygen atoms of $Zn(1)O_5$ or $Zn(2)O_5$ on the basis of the interatomic distances and angles. Furthermore, it is presumed that the bottle-neck is extended according to the size of mobile cation, because the lattice parameters become larger in all directions with an increase in the size of the cation in $M^{II}ZP$ with β-$Fe_2(SO_4)_3$-type structure.[3] Such a unique structure of interstitial sites will accompany ionic conductivity less dependent on the size of the cation for different $M^{II}ZP$ solid electrolytes with β-$Fe_2(SO_4)_3$-type structure.

On the other hand, the mobile cation occupies six coordination site, M(1), which is situated in the octahedra formed by the two triangular faces of two ZrO_6 octahedra (Fig. 3) in M^IZP (or $M^{II}ZP$) with NASICON-type structure.[3,9,10] The distances between the mobile cation and the framework oxygens are almost equal to the sum of octahedrally coordinated Shannon crystal radii, e.g. 2.538(12) Å[9] and 2.810(16) Å[10] for NaZP and KZP, respectively, suggesting a tightly bonded M(1) in the framework. In addition, the bottleneck of the conduction pathway is located near the center of a distorted triangular face of the $M(1)O_6$ octahedra;[11,12] the distortion of the triangular face increases with increasing the ionic radius of the mobile cation.[13] Consequently, the ionic conductivity of the NASICON-type compounds is more dependent on the size of mobile cation.

References

1) P.C. Christidis and P.J. Rentzeperis, Z. Kristallogr., **141**, 233 (1975); M.H. Rapposch, J.B. Anderson, and E. Kostiner, Inorg. Chem., **19**, 3531 (1980); D.C. Craig and N.C. Stephenson, Acta Crystallogr., Sect. B, **24**, 1250 (1968); Y. Piffard, A. Verbaere, and M. Kinoshita, J. Solid State Chem., **71**, 121 (1987).
2) F. d'Yvoire, M.P. Screpel, E. Bretey, and M. Rochere, Solid State Ionics, **9/10**, 851 (1983); Y.K. Naganovsky and S.E. Sigaryov, ibid., **50**, 1 (1992); F. Sudreau, D. Petit, and J.P. Boilot, J. Solid State Chem., **83**, 78 (1989); S. Wang and S.H. Hwu, ibid., **90**, 377 (1991); I.P. Kondratyuk, M.I. Sirota, B.A. Maksimov, L.A. Muradyan, and I. Simonov, Sov. Phys. Crystallogr., **31**, 287 (1986); E.A. Genkina, L.A. Muradyan, and B.A. Maksimov, ibid., **31**, 350 (1986); E.A. Genkina, B.A. Maksimov, S.E. Sigarev, and I.A. Verin, ibid., **36**, 352 (1991); D. Tran Qui and S. Hamdoune, Acta Crystallogr., Sect. C, **43**, 397 (1987); I.A. Verin, E.A. Genkina, B.A. Maksimov, L.A. Muradyan, and M.I. Sirota, Sov. Phys. Crystallogr., **30**, 394 (1985).
3) K. Nomura, S. Ikeda, K. Ito, and H. Einaga, Bull. Chem. Soc. Jpn., **65**, 3221 (1992).
4) K. Nomura, S. Ikeda, K. Ito, and H. Einaga, Solid State Ionics, in press.
5) R.D. Shannon, Acta Crystallogr., Sect. A, **32**, 751 (1976).
6) M. Sljukic, B. Matkovic, B. Prodic, and S. Scavnicar, Croat. Chem. Acta, **39**, 145 (1967).
7) N.P.C. Walker and D. Stuart, Acta. Crystallogr., Sect. A, **39**, 158 (1983).
8) "Solid Electrolytes - General Principles, Characterization, Materials, Applications," ed by P. Hagenmuller and W. Van Gool, Academic Press, New York (1978), Chap. 12.
9) L. Hagman and P. Kierkegaard, Acta Chem. Scand., **22**, 1822 (1968).
10) M. Sljukic, B. Matkovic, B. Prodic, and D. Anderson, Z. Kristallogr., **130**, 148 (1969).
11) H. Kohler and H. Schultz, Mater. Res. Bull., **20**, 1461 (1985).
12) H. Kohler and H. Schultz, Mater. Res. Bull., **21**, 23 (1986).
13) G.E. Lenain, H.A. Mckinstry, J. Alamo, and D.K. Agrawal, J. Mater. Sci., **22**, 17 (1987).

(Received March 8, 1993)