Notes

Bull. Korean Chem. Soc. **2010**, Vol. 31, No. 2   497
DOI 10.5012/bkcs.2010.31.02.497

Synthesis and Characterization of New Pyrochlore-type Oxyfluorides, APbNb$_2$O$_6$F (A = Na and K)

Sung-Chul Kim, Jun-Kun Kang,[†] and Seung-Joo Kim[*]

Department of Chemistry, Division of Energy Systems Research, Ajou University, Suwon 443-749, Korea
[*]E-mail: sjookim@ajou.ac.kr
[†]Institute of NT-IT Fusion Technology, Ajou University, Suwon 443-749, Korea
Received October 16, 2009, Accepted January 6, 2010

The variation of the anion composition *via* partial replacement of oxygen by fluorine has been proven to be a promising way for exploring new compounds, which often leads to a profound modification of the crystal and electronic structures. It has been reported that oxyfluorides show structurally diverse types including perovskite, Ruddlesden-Popper, Dion-Jacobson, fluorite, spinel and scheelite ones, *etc*.[1,2] From the viewpoint of structural chemistry, the compounds with a general formulation $AA'B_2O_6F$ are noticeable because their structures are strongly dependent on the size of atoms in the A and A' sites. An interesting example is the structural transformation from the 3-dimensional pyrochlore to the 2-dimensional perovskite observed in $AA'Nb_2O_6F$ (A = alkali metal, A' = alkaline earths). For small (A, A') atoms the cubic pyrochlore structures are predominant as observed in the cases of LiCaNb$_2$O$_6$F,[3] NaCaNb$_2$O$_6$F[4], and KCaNb$_2$O$_6$F,[5] whereas the layered perovskites are the most stable structure for large (A, A') atoms as in KSrNb$_2$O$_6$F [6] and RbSrNb$_2$O$_6$F.[7] As an extension of these researches, we have tried to substitute various atom pairs for the A and A' sites. Here we report the syntheses of new transition-metal oxyfluorides, APbNb$_2$O$_6$F (A = Na and K) and their crystal structures determined using synchrotron X-ray powder diffraction. Pb-containing compounds are intriguing for the researchers to develop visible-light-sensitive photocatalysts because of their narrow energy band gap. In this work, we also discuss the relationship between structure and band gap in this oxyfluoride system based on the diffuse reflectance spectra.

The powder X-ray diffraction patterns for both compounds, NaPbNb$_2$O$_6$F and KPbNb$_2$O$_6$F showed the cubic symmetry with lattice parameter a = 10.5595(5) Å and a = 10.5911(6) Å, respectively. Any additional peaks due to symmetry lowering or impurity phase were not detected. Systematic absences suggested two possible cubic space groups, viz. centrosymmetric Fd-$3m$ (No. 227) and non-centrosymmetric Fd-3 (No. 203). Both space groups turned out later to give basically the same structure solution. Thus, the higher symmetric Fd-$3m$ was chosen. The positions of the relatively heavy atoms (Na, K, Pb, and Nb) were determined employing direct methods using the SXRD data, for which a total of 67 and 69 'F_{obs}' amplitude factors for NaPbNb$_2$O$_6$F and KPbNb$_2$O$_6$F, respectively, were converted into structure factors and used as an input for SHELXS97.[8] Na (or K) and Pb atoms are distributed statistically over the same crystallographic position (Wyckoff site *16d*) with

an occupancy of 1/2 for each atom. Nb atoms are located at *16c* sites. After this step, the cations were removed from the refinement and the residual density was calculated. The difference Fourier maps indicated that the anions were located at *8b* and *48f*. During the refinement it was assumed that the fluorine atoms occupied *8b* sites and the oxygen atoms occupied *48f* sites. The ordered distribution of fluorine and oxygen atoms in the oxyfluoride lattice was confirmed by Bond Valence Sum (BVS) calculation. The BVS values were 0.95 and 2.02 for fluorine and oxygen in NaPbNb$_2$O$_6$F. Likewise, the BVS values were 0.93 and 2.04 for fluorine and oxygen in KPbNb$_2$O$_6$F. The BVS values very close to the formal charges of F$^-$ ion and O^{2-} ion provide a clear evidence of the ordered anion distribution. The structure parameters (lattice parameters, refined atomic positions and isotropic temperature factors for all atoms) and residual indices are summarized in Table 1. The observed, calculated and difference patterns from the Rietveld refinements plots for SXPDs are shown in Fig. 1.

In the structure of APbNb$_2$O$_6$F, the (A, Pb) atoms are coordinated to two F atoms and six O atoms, forming a puckered hexagonal bipyramid which is axially compressed with the two

Table 1. Crystallographic data of NaPbNb$_2$O$_6$F and KPbNb$_2$O$_6$F refined from synchrotron X-ray powder diffraction. (λ = 1.5498 Å, T = 298 K)

	NaPbNb$_2$O$_6$F	KPbNb$_2$O$_6$F
Crystal system	Cubic	
Space group	Fd-$3m$	
Cell parameter a (Å)	10.5595(5)	10.5911(6)
Volume (Å^3)	1177.42(10)	1188.02(12)
Z	8	
x	0.3123(6)	0.3100(9)
B$_{A/Pb}$ (100 Å^2)	1.47(3)	1.94(5)
B$_{Nb}$ (100 Å^2)	0.71(3)	0.72(4)
B$_O$ (100 Å^2)	0.59(10)	1.18(17)
B$_F$ (100 Å^2)	2.3(4)	2.0(4)
R$_p$	12.0%	15.2%
R$_{wp}$	15.6%	20.8%
R$_{exp}$	8.58%	9.01%
R$_{Bragg}$	2.67%	4.64%
χ^2	3.31	5.32

[*]Atomic positions: *16d* (0.5, 0.5, 0.5) for Na(K)/Pb, *16c* (0, 0, 0) for Nb, *48f* (x, 1/8, 1/8) for O and *8b* (3/8, 3/8, 3/8) for the F atoms.
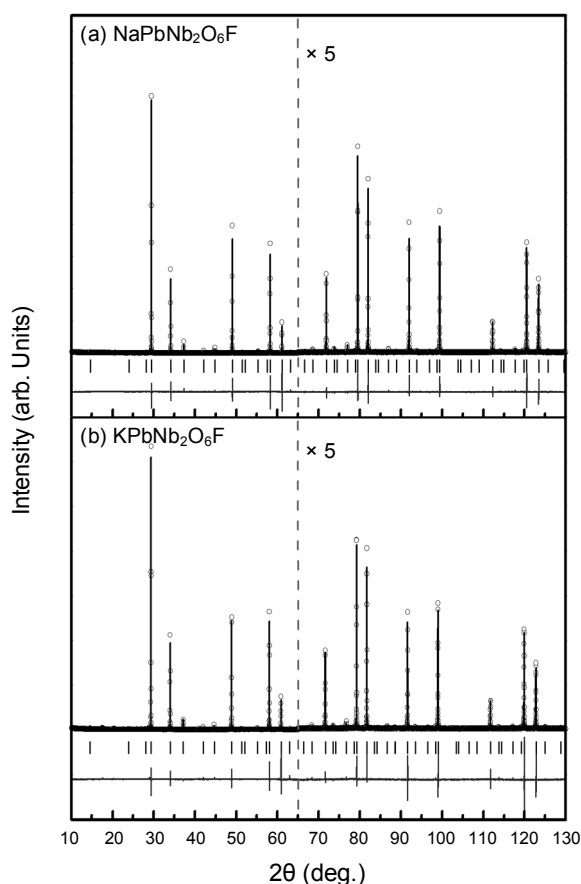
Figure 1. Observed (open circles), calculated (line) and difference (bottom) synchrotron X-ray diffraction patterns for (a) $NaPbNb_2O_6F$ and (b) $KPbNb_2O_6F$. Vertical bars indicate calculated positions of Bragg peaks (The peak intensities over 65 degrees in 2θ have been magnified 5 times).
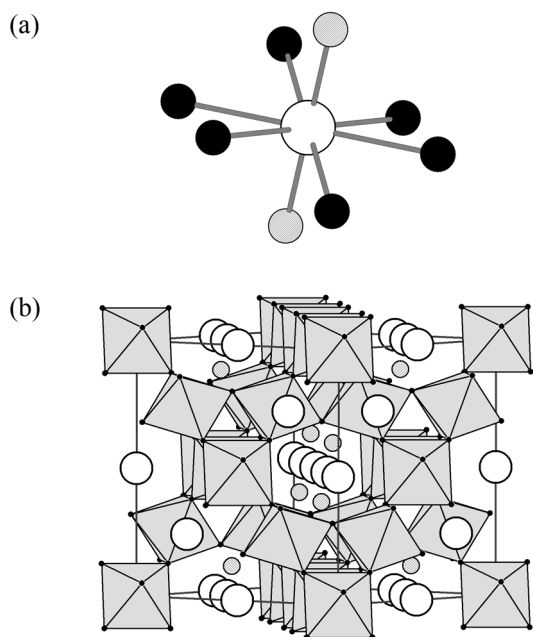

Figure 2. Schematic views of (a) Na/Pb local structure and (b) $NaPb$-Nb_2O_6F structure, showing Na/Pb (large sphere), F (gray sphere), O (dark sphere) and NbO_6 octahedra.

Table 2. Interatomic distances and angle for $NaPbNb_2O_6F$ and $KPbNb_2O_6F$.

	$NaPbNb_2O_6F$	$KPbNb_2O_6F$
A/Pb-O (Å)	2.723(3) × 6	2.749(7) × 6
A/Pb-F (Å)	2.286(1) × 2	2.293(1) × 2
Nb-O (Å)	1.979(4) × 6	1.977(3) × 6
Nb-O-Nb (°)	141.2(1)	142.5(1)
A/Pb-F-A/Pb (°)	109.5(1)	109.5(1)

F atoms being at considerably shorter distance than the six O atoms (Fig. 2a). The Nb atom is bonded to six O atoms at equal distances in octahedron. The NbO_6 octahedron is connected to the six others *via* corner-sharing of oxygen atoms. By neglecting the A/Pb-O interaction the $APbNb_2O_6F$ structures can be regarded as interpenetrating networks of $[Nb_2O_6]^{2+}$ and $[APbF]^{2+}$ units as shown in Fig. 2b. The Nb-O bond lengths (*c.a.* 1.98 Å) are nearly identical for both compounds, whereas the Nb-O-Nb bond angle for $KPbNb_2O_6F$ is slightly larger than that for $NaPbNb_2O_6F$ (Table 2).

The title compounds are isostructural with the previously reported pyrochlore oxyfluorides such as $NaCaNb_2O_6F$, $KCaNb_2O_6F$, and $NaSrNb_2O_6F$.[4,5,9] The local structure around Pb atom is nearly identical with those in Ca or Sr atoms in the pyrochlore compounds. For example, the K/Pb-F bond length in $KPbNb_2O_6F$ (2.293 Å) is comparable to the K/Ca-F bond length in $KCaNb_2O_6F$ (2.285 Å).[5] The K/Pb-O bond length (2.749 Å) is somewhat larger than the K/Ca-O bond length (2.701 Å), which is consistent with the larger ionic radius of Pb^{2+} (r = 1.29 Å) than that of Ca^{2+} (r = 1.12 Å). A notable point here is that the Pb-containing compounds prefer the pyrochlore structure to the layered perovskite one in spite of the large size of Pb^{2+} ion. It has been known that the $AA'Nb_2O_6F$ compound with large (A, A') atoms tends to have the layered perovskite structure as shown in the case of $KSrNb_2O_6F$. Although the ionic radius of Pb^{2+} is larger than that of Sr^{2+} (r = 1.21 Å), the preference for pyrochlore structure underlines that the electronic structure of Pb^{2+} ($d^{10}s^2$) also significantly affects the structural stability.

UV-vis diffuse reflectance spectra of $APbNb_2O_6F$ are compared with those of the isostructural compounds, $ACaNb_2O_6F$ (A = Na and K) in Fig. 3. The $ACaNb_2O_6F$ absorbs light in the UV region, whereas the Pb-containing compound, $APbNb_2O_6F$ shows obviously red-shifted absorption. The energy band gaps were estimated from the steep edges of absorption spectra; the values were 4.07 eV for $NaCaNb_2O_6F$, 4.00 eV for $KCaNb_2O_6F$, 3.20 eV for $NaPbNb_2O_6F$ and 3.05 eV for $KPbNb_2O_6F$, respectively. Since all the compounds contain NbO_6 octahedra, it can be thought that the conduction and valence bands consist of empty Nb 4d and occupied O 2p orbitals, respectively. The O 2p orbitals, however, is effectively hybridized with 6s^2 orbital of Pb^{2+}. The hybridization of Pb 6s and O 2p orbitals would push up the position of the valence band, giving the smaller band gap compared to compound that does not contain Pb in its structure. Similar aspects have been observed in several semiconductors that contain metal ions with nd^{10} or ns^2 outer layer electron configurations (such as Ag^+, Bi^{3+} and Sn^{2+}).[10-13] It is also notable

Notes

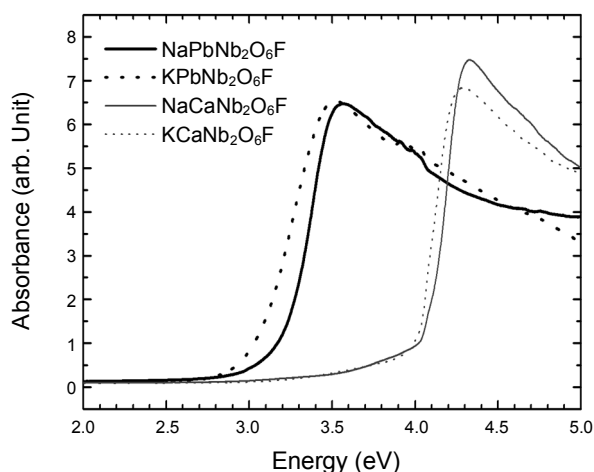*Bull. Korean Chem. Soc.* **2010**, Vol. 31, No. 2   499

Figure 3. UV-vis reflectance spectra of APbNb$_2$O$_6$F and comparison with ACaNb$_2$O$_6$F (A = Na and K).

that the replacement of Na by K in the A site leads to an additional reduction of band gap. The smaller band gaps of K-containing compounds compared to Na-containing ones ($\Delta E_g = -0.07$ eV for ACaNb$_2$O$_6$F and $\Delta E_g = -0.15$ eV for APbNb$_2$O$_6$F) may be due to the different electronegativities for K and Na atoms. From the viewpoint of bond competition, the more electropositive K atom can be expected to make the adjacent Nb-O bond have strong covalency and to give the smaller band gap in the K-containing compounds.

Conclusively, the Pb-containing oxyfluorides, APbNb$_2$O$_6$F (A = Na or K) with the cubic pyrochlore structure exhibited the energy band gaps of about 3 eV which were significantly smaller than those of ACaNb$_2$O$_6$F (≈ 4 eV). The band gap was also affected finely by the replacement of A atoms. The present results would be applicable to the design of new photocatalyst working under visible light.

Experimentals

Polycrystalline APbNb$_2$O$_6$F samples were prepared by solid-state reaction of AF (A = Na and K) and PbNb$_2$O$_6$. The precursor, PbNb$_2$O$_6$ was prepared by firing the stoichiometric mixture of PbO and Nb$_2$O$_5$ at 1273 K for 12 h. The mixtures of PbNb$_2$O$_6$ and AF were pressed into pellets in a glove box under the anhydrous Ar atmosphere, and then placed inside sealed gold tubes. The tubes were sealed using a propane/O$_2$ flame and heated at 1023 K for 12 h. After cooling to room temperature, the ivory-colored products were removed from the tubes.

The composition of the products were confirmed with energy-dispersive X-ray analysis (JEOL JSM-5600 scanning electron microscope fitted with a Be window detector, Oxford Instrument). The ratio of atoms was matched with the nominal composition within the experimental error range (within 5% for cations and 10% for anions) for the both compounds.

Synchrotron X-ray powder diffraction (SXRD) measurement was performed on beamline 8C2-HRPD at Pohang Accelerator Laboratory, Pohang, Korea. The incident X-rays were vertically collimated by a mirror, and monochromated to the wavelength of 1.5498 Å by a double-crystal Si(111) monochromator. Datasets were collected in the range of $10° \leq 2\theta \leq 130°$ with a step size of $0.01°$ (2θ angle). Reflections of the compounds were indexed using McMaille software and checked with the DICVOL program.[14] The whole SXRD patterns were fit using the Le Bail method.[15] Refinement of atomic positions and isotropic displacement parameters were carried out by the Rietveld method using the Fullprof program with pseudo-Voigt peak shapes.[16]

Diffuse reflectance data were collected over the range 200 - 800 nm using a UV-vis spectrophotometer (Shimadzu UV-2400 PC). BaSO$_4$ was used as a reference. The data were transformed into absorbance using the Kubelka-Munk function.[17]

References

1. Wells, A. F. *Structural Inorganic Chemistry*; 5th ed.; Oxford Univ. Press: Oxford, 1984.
2. Subramanian, M. A.; Aravamudan, G.; Subba Rao, G. V. *Prog. Solid State Chem.* **1983**, *15*, 55.
3. Le Berre, F.; Crosnier-Lopez, M.; Galven, C.; Fourquet, J.; Legein, C.; Body, M.; Buzare, J. *Dalton Trans.* **2007**, 2457.
4. Von Gaertner, H. R. *Geologie und Palaeontologie. Beilagen, Abt. A* **1930**, *61*, 1.
5. Yoo, C. Y.; Kim, S. J. *Acta Cryst.* **2007**, *E63*, i203.
6. Yoo, C. Y.; Hong, K. P.; Kim, S. J. *Acta Cryst.* **2007**, *C63*, i63.
7. Choy, J. H.; Kim, J. Y.; Kim, S. J.; Sohn, J. S.; Han, O. H. *Chem. Mater.* **2001**, *13*, 906.
8. Sheldrick, G. M. *Acta Cryst.* **2008**, *A64,* 112.
9. Yoo, C. Y.; Kim, S. J. *J. Phys. Chem. Solids* **2008**, *69*, 1475.
10. Kato, H.; Kobayashi, H.; Kudo, A. *J. Phys. Chem.* **2002**, *B106*, 12441.
11. Yao, W.; Te, J. *J. Phys. Chem.* **2005**, *B110*, 11188.
12. Hosogi, Y.; Tanabem, K.; Kato, H.; Kobayashi, H.; Kudo, A. *Chem. Lett.* **2004**, *33*, 28.
13. Kim, H. G.; Hwang, D. W.; Lee, J. S. *J. Am. Chem. Soc.* **2004**, *126*, 8912.
14. Boultif, A.; Louer, D. *J. Appl. Cryst.* **2004**, *37*, 724.
15. Le Bail, A.; Duroy, H.; Fourquet, J. L. *Mat. Res. Bull.* **1988**, *23*, 447.
16. Rodriguez-Carvajal, J. *FULLPROF. Commission on Powder Diffraction (IUCr), Newsletter* **2001**, *26*, 12.
17. Kubelka, P.; Munk, F. *Z. Tech. Phys.* **1931**, *12*, 593.