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Crystal structures of new layered perovskite-type oxyfluorides, $CsANb_2O_6F$ (A = Sr and Ca) and comparison with pyrochlore-type $CsNb_2O_5F$

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ABSTRACT

New layered perovskite-type oxyfluorides, $CsSrNb_2O_6F$ and $CsCaNb_2O_6F$, were prepared *via* solid state reactions and their crystal/electronic structures were compared to those of a compositional analogue, $CsNb_2O_5F$ which has a 3-dimensional pyrochlore-type structure. The $CsSrNb_2O_6F$ and $CsCaNb_2O_6F$ phases are derived from the *Dion-Jacobson* family of a general formula $A[A'_{n-1}B_nX_{3n+1}]$ with $n = 2$. Rietveld refinements based on synchrotron X-ray diffraction data revealed that $CsSrNb_2O_6F$ belongs to the tetragonal system with $a = 3.86716(1)$ Å, $c = 11.45257(2)$ Å ($P4/mmm$, $Z = 1$), while $CsCaNb_2O_6F$ adopts a $2a_p \times 2a_p \times 2c_p$ superstructure with orthorhombic unit cell parameters, $a = 7.64813(1)$ Å, $b = 7.67516(1)$ Å, $c = 22.43663(3)$ Å ($Bmmb$, $Z = 8$). The anion distributions in the lattices were confirmed by applying *Bond Valence Sum* (*BVS*) method; the F^- ions occupy the central sites of the corner-sharing double perovskite block in the layered structures, but no ordering of anions was found in the pyrochlore structure. Through UV–Vis diffuse reflectance measurement, the band gap energy was estimated to 3.43 eV for $CsSrNb_2O_6F$, 3.65 eV for $CsCaNb_2O_6F$ and 4.00 eV for $CsNb_2O_5F$. The band gap energy showed a good correlation with the Nb-O(F)-Nb bond angle(θ) in the oxyfluorides. As the Nb-O(F)-Nb bond angle deviates from 180°, the value of E_g increase. The good linearity observed in the E_g *vs.* $\cos(180 - \theta)$ plot suggests that E_g can be finely controlled by adjusting of the Nb-O(F)-Nb bond angle in the lattice.

1. Introduction

Layered perovskite-type compounds belonging to *Dion-Jacobson* (*DJ*) series, $AA'_{n-1}B_nX_{3n+1}$ (A = alkaline metal, A' = alkaline-earth or lanthanide metal, and B = transition metal, X = mainly oxygen, $2 \le n \le 4$) have been attracted much attention because of their interesting physicochemical properties such as ion-exchange ability [1–3], intercalation reaction [4,5], exfoliation behavior [6,7], ionic conductivity [8,9] and photocatalytic activity [10,11]. In these phases, n defines the number of BX_6 octahedra forming perovskite slabs which are separated by A cations located to inter-space between perovskite slabs and A' cations occupy the 12-coordinate perovskite cage. Due to the compositional diversity of this family, the design and synthesis of new compounds is still challenging. One promising approach to derive new compound is a partial substitution of anions. The fluoride (F^-) ions are very similar in size with the oxide (O^{2-}) ion, which can be used to stabilize an isotypic structure having different composition by simultaneous substitution of appropriate cation to compensate for the charge difference of the anions. The first *DJ*-type oxyfluoride derived from this manner is $RbSrNb_2O_6F$ [12] which is isotypic with the well-known *DJ*-type oxide, $RbLaNb_2O_7$ [13]. This synthetic strategy has been extended to other compositions: $RbLnTiNbO_6F$ (Ln = La, Pr, and Nd) [14], and $KSrNb_2O_6F$ [15].

In addition of the layered perovskite-type structure, the pyrochlore-related structures are also an important class in the oxyfluorides, as the name “pyrochlore” was originated from a mineral oxyfluoride, $(NaCa)(Nb,Ta)_2O_6(OH/F)$ [16]. The Nb-containing pyrochlore compounds such as $AA'Nb_2O_6F$ (A = Li, Na, K for A'= Ca and Pb; A = Li, Na for A'= Sr) was reported to date [17–20]. Although the pyrochlore and *DJ*-type compounds ($n = 2$) are similar in composition, their crystal structures are significantly different from each other. The pyrochlore structure is described as an interpenetrating network of NbO_6 octahedra and (AA') F chains. In general, the pyrochlore contains small cations such as Na^+ and Ca^{2+} located at A, and A' sites, while the layered *DJ*–type structures can be stabilized by large cations such as Rb^+ and Sr^{2+} [17]. Other compositional analogue, ANb_2O_5F (A = Rb, and Cs) also

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Table 1
Crystal data and structure refinement for $CsSrNb_2O_6F$, $CsCaNb_2O_6F$, and $CsNb_2O_5F$ refined from synchrotron X-ray diffraction.

	$CsSrNb_2O_6F$	$CsCaNb_2O_6F$	$CsNb_2O_5F$
Formula weight (M_r)	521.35	473.79	417.71
Space group	*P4/mmm*	*Bmmb*	*Fd–3m*
Z	1	8	8
a (Å)	3.86716(1)	7.64813(1)	10.52885(1)
b (Å)	3.86716(1)	7.67516(1)	10.52885(1)
c (Å)	11.45257(2)	22.43663(3)	10.52885(1)
V (Å^3)	171.272(1)	1317.045(3)	1167.193(2)
Density (g/cm^3)	5.055	4.779	4.754
Wavelength (Å)	1.5498	1.5498	1.549
Step scan increment (°, 2θ)	0.01	0.01	0.01
2θ range (°)	10–131	10–131	10–131
Temperature (K)	298	298	298
No. of reflections	127	655	67
No. of structural parameters (*P*1)	15	34	10
No. of profile parameters (*P*2)	7	8	6
$R_p = (\Sigma\lvert y(obs)-y(calc)\rvert)/\Sigma y(obs)$	13.1%	15.3%	13.1%
$R_{wp} = [(\Sigma w[y(obs)-y(calc)]^2/\Sigma wy^2(obs)]^{1/2}$	17.7%	20.7%	17.3%
$R_{exp} = [(N-P1-P2)/\Sigma wy^2(obs)]^{1/2}$	12.3%	12.7%	12.0%
$R_{bragg} = (\Sigma\lvert I(obs)-I(calc)\rvert)/\Sigma I(obs)$	6.77%	7.01%	4.75%
$\chi^2 = (R_{wp}/R_{exp})^2$	2.06	2.66	2.06

Table 2
Atomic coordinates and equivalent isotropic displacement parameters for $CsSrNb_2O_6F$, $CsCaNb_2O_6F$ and $CsNb_2O_5F$.

	Site	Occ.	*x*	*y*	*z*	*B*(x100 Å^2)
$CsSrNb_2O_6F$						
Cs1	1*d*	1	0.5	0.5	0.5	1.21(2)
Sr1	1*c*	1	0.5	0.5	0	0.42(2)
Nb1	2*g*	1	0	0	0.20723(8)	0.16(1)
O1	4*i*	1	0	0.5	0.1660(4)	0.36(7)
O2	2*g*	1	0	0	0.3625(6)	0.36(7)
F1	1*a*	1	0	0	0	1.0(1)
$CsCaNb_2O_6F$						
Cs1	4*c*	1	0	0.25	0.2611(1)	1.21(9)
Cs2	4*c*	1	0.5	0.25	0.2371(1)	0.98(8)
Ca1	4*c*	1	0	0.25	0.0039(6)	0.4(1)
Ca2	4*c*	1	0.5	0.25	0.0072(5)	0.8(1)
Nb1	16*h*	1	0.2450(1)	− 0.0007(4)	0.10219(4)	0.10(1)
O1	16*h*	1	0.208(1)	− 0.012(2)	0.1807(3)	0.5(1)
O2	8*g*	1	0.227(2)	0.25	0.0796(8)	0.5(1)
O3	8*g*	1	0.269(2)	0.75	0.0791(8)	0.5(1)
O4	8*f*	1	0	− 0.017(2)	0.0691(5)	0.5(1)
O5	8*f*	1	0.5	0.029(2)	0.1001(5)	0.5(1)
F1	8*e*	1	0.309(1)	0	0	0.7(2)
$CsNb_2O_5F$						
Cs1	8*b*	1	0.375	0.375	0.375	2.87(5)
Nb1	16*c*	1	0	0	0	2.08(4)
O1	48*f*	5/6	0.3115(8)	0.125	0.125	0.95(1)
F1	48*f*	1/6	0.3115(8)	0.125	0.125	0.95(1)

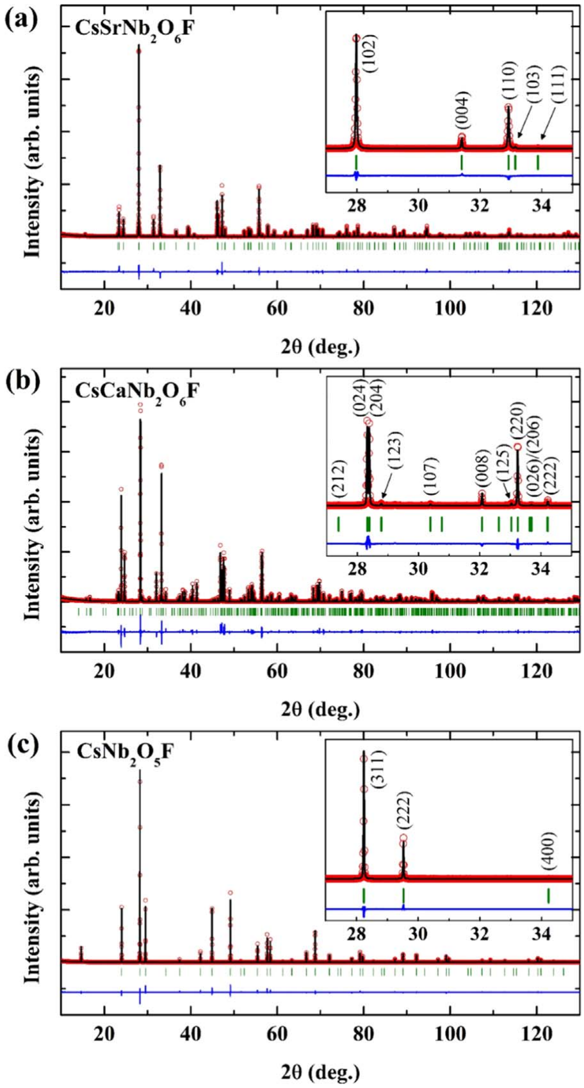

Fig. 1. Rietveld refinement of the (a) $CsSrNb_2O_6F$, (b) $CsCaNb_2O_6F$ and (c) $CsNb_2O_5F$ based on synchrotron X-ray diffraction data. Measured data, fitted results, expected reflection positions, and the difference between measured and fitted results are expressed as red hollow circles, black lines, green vertical lines, and blue solid lines, respectively. The insets show the indexation of the selected portion of the diffraction patterns. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

exhibits a pyrochlore-related structure in which the A′ site and one other anion site are empty compared to the ideal perovskite. This structure is called "defective pyrochlore-type" [21].

In this research, we describe the syntheses and the crystal structures of new *DJ*-type oxyfluorides, $CsANb_2O_6F$ (*A* = Sr and Ca). These oxyfluorides were derived from a well-known oxide, $CsLaNb_2O_7$ by replacements of O^{2-} and La^{3+} ions with F^- and Sr^{2+} (Ca^{2+}) ions [22]. $CsSrNb_2O_6F$ has a tetragonal unit cell (*a* ~ 3.85 Å and *c* ~ 11.3 Å), which is isotypic with $RbSrNb_2O_6F$ [12]. The primitive tetragonal structure, however, could not be adopted in $CsCaNb_2O_6F$ because several superlattice peaks were found in the preliminary X-ray diffraction (XRD) patterns, indicating an enlargement of the unit cell which may be resulted from structural distortion. Since such distortions often arise from subtle displacements of oxygen/fluorine atoms (including 'octahedral tilt' type behavior) it is hard to determine the precise structure only with conventional XRD method. Here the structures of $CsANb_2O_6F$ (*A* = Sr, and Ca) are investigated by synchrotron X-ray diffraction (*s*XRD) measurements and compare with that of a defective pyrochlore-type $CsNb_2O_5F$. We also elucidated the correlation between the local structure and the band gap energy in the oxyfluorides.

2. Experimental

Polycrystalline $CsSrNb_2O_6F$, $CsCaNb_2O_6F$ and $CsNb_2O_5F$ compounds were prepared using solid-state reaction of mixtures of CsF with either $SrNb_2O_6$, $CaNb_2O_6$ or Nb_2O_5. The precursors, $SrNb_2O_6$ and $CaNb_2O_6$ were obtained by firing the stoichiometric quantities of high-purity $SrCO_3$ or $CaCO_3$ and Nb_2O_5 at 1373 K for 2 days. Then $SrNb_2O_6$, $CaNb_2O_6$ or Nb_2O_5 was well mixed with CsF and pressed into pellets under an anhydrous argon atmosphere in a glovebox. The pellets were placed in tubes, sealed and heated for 12 h. The heating temperatures were 973 K for $CsSrNb_2O_6F$, 1093 K for $CsCaNb_2O_6F$ and 973 K for $CsNb_2O_5F$.