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Facile synthetic route to transition metal oxyfluorides via reactions between metal oxides and PTFE

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ABSTRACT

Inorganic oxyfluorides have significant importance in the development of new functionalities for energy production and storage, photonics, catalysis, etc. In order to explore a simple preparation route that avoids the use of toxic HF or F_2 gas as a reaction reagent, we have employed polytetrafluoroethylene (PTFE). Five oxyfluorides including $Nb_5O_{12}F$, Nb_3O_7F, Ta_3O_7F, TaO_2F, and $Mo_4O_{11.2}F_{0.8}$ were synthesized by reactions between PTFE and transition metal oxides in sealed quartz ampules. The reaction mechanism was studied by means of gas analysis, which detected SiF_4 as a main product gas during the reaction. A possible reaction mechanism between the PTFE and transition metal oxides is discussed.

1. Introduction

Transition metal oxides provide us with an important group of compounds having interesting physical properties and valuable functionalities. Recently, a series of progress has been made in enhancing the functionality of transition metal oxides by substituting fluorine for oxygen ions; they are neighbors in periodic table. The aliovalent nature of F^- and O^{2-} ions allows one to introduce electrons into the conduction band of the parent compound by the substitution. The similar ionic radii of them are advantageous in minimizing the resulting lattice deformation. One of marked effects of fluorination was found in insulating WO_3 which was rendered metallic and even superconducting below 0.4 K at high fluorine content [1].

Oxyfluorides containing both oxygen and fluorine as main constituent elements have attracted increasing attention, which are typical mixed anion compounds [2]. The introduction of highly electronegative fluorine causes a significant change in the magnitude of band gap. For example, Nb_2O_5 is one of the promising photocatalysts because of its wide variety and efficient catalytic activities [3–5]. However, because of the large band gap of 3.4 eV, Nb_2O_5-based photocatalysts can be used only under ultraviolet light irradiation which constitutes only a small fraction ($< 5\%$) of the solar spectrum. In order to utilize solar energy efficiently, a reduction of the band gap to the visible-light energy is needed. Such a reduction of the band gap has indeed been achieved in some niobium oxyfluorides. A smaller band gap of 3.2 eV is realized in NbO_2F, and Ag-inserted NbO_2F shows a visible-light photocatalytic activity [6]. Moreover, Nb_3O_7F has a band gap of 2.9 eV, and the rate constant of photocatalytic activity of nanostructured Nb_3O_7F is larger than that of commercial TiO_2 [7]. On one hand, an enhancement in ionic conductivity is observed in some oxyfluorides like $Ba_{2-0.5x}In_2O_{5-x}F_x$ [8], and an anisotropic ionic conductivity is expected from a specific ordering of different anions in mixed anion compounds in the Ruddlesden-Popper, Dion-Jacobson, and Aurivillius type oxyfluoride families [2]. It is expected that oxyfluorides have very different properties from oxides because of the different electronic structures originating from the crystal field of multiple anions.

Reactions of oxides with hydrofluoric acid (HF) or fluorine gas (F_2) have been employed for fluorine doping or synthesis of oxyfluorides. However, a special care is needed in handling toxic HF or F_2 gas. Alternatively, a more facile and safe route of fluorination through reactions of an oxide with an organic polymer containing fluorine has been investigated recently. The organic polymer can be a promising fluorination agent owing to two characteristics; chemical stability at room temperature and relatively low decomposition temperatures compared with inorganic compounds. In addition, carbon contained in organic polymers may work to reduce oxides at elevated temperatures and can assist fluorination, which enable us to perform fluorine substitution under milder conditions. The fluorination method using polymers has been used to synthesize several layered oxyfluorides including $Sr_2TiO_3F_2$ [9], $Ca_2CuO_2F_2$ [9], $SrFeO_2F$ [10], and $RbLaNb_2O_6F$ [11]. Although the method is efficient, the actual reaction process is often complicated, and the underlying mechanism has been rarely investigated to date. Moreover, the application of polymer fluorination has been limited to layered compounds thus far, and the validity of

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Table 1
Nominal molar F/O ratio, reaction temperature, products, crystal structure and lattice parameters for oxyfluorides synthesized in this study.

Starting oxide	Molar F/O	Temp.(°C)	Products	Crystalstructure	Lattice parameters	
					This work	Literature values
Nb_2O_5	0.5	900	$Nb_5O_{12}F$	Orthorhombic (*Ammm*)	$a = 3.924(1)$ Å $b = 6.157(2)$ Å $c = 3.6579(8)$ Å	$a = 3.936(3)$ Å $b = 6.153(2)$ Å $c = 3.656(1)$ Å
Nb_2O_5	2.5	900	Nb_3O_7F	Orthorhombic (*Cmmm*)	$a = 20.679(4)$ Å $b = 3.834(1)$ Å $c = 3.926(1)$ Å	$a = 20.67$ Å $b = 3.833$ Å $c = 3.927$ Å
Ta_2O_5	1.0	600	Ta_3O_7F	Orthorhombic (*Cmmm*)	$a = 6.425(19)$ Å $b = 10.54(6)$ Å $c = 3.910(15)$ Å	$a = 6.478(3)$ Å $b = 10.496(3)$ Å $c = 3.907(2)$ Å
Ta_2O_5	1.0	500 (mix)	TaO_2F	Cubic ($Pm\bar{3}m$)	$a = 3.8966(1)$ Å	$a = 3.896(3)$ Å
MoO_3	0.2	500	$Mo_4O_{11.2}F_{0.8}$	Orthorhombic (*Cmcm*)	$a = 3.887(1)$ Å $b = 14.060(3)$ Å $c = 3.717(1)$ Å	$a = 3.878(4)$ Å $b = 13.96(1)$ Å $c = 3.732(5)$ Å

other types of compounds is not known. Thus, it is important to investigate the mechanism and to examine what kind of oxyfluorides can be synthesized by the polymer fluorination method.

Here, we have investigated the reactions of binary transition metal oxides, such as Nb_2O_5, Ta_2O_5, and MoO_3, with polytetrafluoroethylene [PTFE; -$(CF_2\text{-}CF_2)_n$-] in order to demonstrate the applicability of the PTFE fluorination method. Previously reported syntheses using PTFE suffered from a poor control of fluorine concentration because the reactions were performed in flowing inert gas. In this work, fluorination was done in a sealed quartz ampule in order to control fluorination precisely and achieve higher fluorine content in the product. Five oxyfluorides including $Nb_5O_{12}F$, Nb_3O_7F, Ta_3O_7F, TaO_2F, and $Mo_4O_{11.2}F_{0.8}$ were synthesized successfully. The results of fluorination are summarized in Table 1.The synthetic conditions were found to depend on the starting transition metal oxides. This facile route to transition metal oxyfluorides using PTFE may be applied to other systems and would be useful to explore functional oxyfluorides.

2. Results and discussion

2.1. Fluorination of Nb_2O_5

Several niobium oxyfluorides are known to date: a homologous series $Nb_nO_{2n\text{-}1}F_{n+2}$ ($n = 1$ [12], 3 [13], and ∞ [14,15]), Nb_3O_7F, and $Nb_5O_{12}F$ [16]. Moreover, a new compound $Nb_2O_2F_3$ [17] was discovered in 2015. Most of them were synthesized by using HF. We synthesized Nb_3O_7F and $Nb_5O_{12}F$ by the reaction of Nb_2O_5 with PTFE in an evacuated quartz ampule. At first, the optimum reaction temperature was determined by comparing products sintered at various temperatures from a nominal fluorine to oxygen ratio of $F/O = 0.25$. As shown in the XRD patterns of Fig. 1a, the XRD peaks from Nb_2O_5 remain unchanged when sintered at 500 and 700 °C, while the relative intensities of the peaks at 22.6°, 28.3°, and 29° probably from the oxyfluoride $Nb_5O_{12}F$ increase in the sample reacted at 900 °C. Thus, fluorine substitution becomes effective at high temperatures above ~900 °C. Since the samples reacted above 900 °C obviously look inhomogeneous, the optimum sintering temperature for Nb_2O_5 was set to 900 °C. The optimum reaction temperature was found to depend on the starting oxide. For example, the optimum reaction temperature for WO_3 is 550 °C, because reduction of WO_3 occurs to produce WO_2 as a by-product at temperatures above 600 °C.

For the next step, the nominal content of PTFE was increased at a fixed sintering temperature of 900 °C. The XRD patterns of the products show a systematic variation with increasing the nominal F/O ratio, as shown in Fig. 1b. First, the XRD peaks between 24° and 26° from Nb_2O_5 get weak and completely disappear at $F/O = 0.5$, while new reflections at 22.6°, 28.3°, and 29° grow with increasing nominal F/O ratio. With further increasing the F/O ratio, those reflections at 28.3° and 29° are replaced by another set of peaks at around 26° and 32°. The XRD pattern remained unchanged when the nominal F/O ratio was further increased. As shown in Fig. 1c, all the peaks of the XRD pattern for $F/O = 0.5$ can be indexed to an orthorhombic cell (Space group *Ammm*) with lattice constants of $a = 3.924(1)$ Å, $b = 6.157(2)$ Å, and $c = 3.6579(8)$ Å. This XRD pattern is nicely matched with that of $Nb_5O_{12}F$ (orthorhombic, $a = 6.15$ Å, $b = 18.29 = 3.658 \times 5$ Å, $c = 3.92$ Å) [16]; the recent structural analysis using a single crystal of $Nb_5O_{12}F$ revealed that the true structure is an incommensurately modulated variant of the UO_3 structure (Superspace group X:*Pmmm* (00γ):1s-1; $a = 3.936(3)$ Å, $b = 6.153(2)$ Å, $c_1 = 3.656(1)$ Å, $c_2 = 2.28$ Å, modulation wave vectors $q_1 = 1.61\ c_0$, $q_2 = 0.62\ c_2$) [18]. On the other hand, the XRD pattern for $F/O = 2.5$ sample (Fig. 1d) is indexed in an orthorhombic cell (Space group *Cmmm*) with cell parameters $a = 20.679(4)$ Å, $b = 3.834(1)$ Å, and $c = 3.926(1)$ Å. The space group and cell parameters are consistent with those of the oxyfluoride Nb_3O_7F (Space group *Cmmm*, $a = 20.67$ Å, $b = 3.833$ Å, $c = 3.927$ Å) [16]. Since no other peaks are observed, Nb_3O_7F is obtained as a single phase. It is reasonable that monophasic Nb_3O_7F is produced at the large F/O ratio of 2.5 instead of $Nb_5O_{12}F$. The F/O ratio in $Nb_5O_{12}F$ and Nb_3O_7F are 8.3% and 14.3%, respectively, which are much smaller than the nominal F/O ratios. Thus, excess amount of PTFE is needed in this fluorination method.

In the previous study, Nb_3O_7F and $Nb_5O_{12}F$ were synthesized by solid state reactions at 800 °C from Nb_2O_5 and NbO_2F at ratios of 1:1 and 2:1, respectively [16,18]. Andersson et al. also sintered Nb_2O_5 and NbO_2F at ratios of n:1 ($n = 1.5$, 2.5, 3, 4, 5), but, no other oxyfluoride phases were obtained. Thus, Nb_3O_7F and $Nb_5O_{12}F$ may be thermodynamically stable in the Nb-O-F system. Our PTFE method makes it possible to synthesize them in a feasible way. Other oxyfluorides with high fluorine content like the homologous series $Nb_nO_{2n\text{-}1}F_{n+2}$ and $Nb_2O_2F_3$ were not synthesized in this method.

The valence state of Nb ions in both Nb_3O_7F and $Nb_5O_{12}F$ is 5+ in the electronic configuration of $4d^0$. Thus, they should be white in powder and transparent in crystal. However, our Nb_3O_7F and $Nb_5O_{12}F$ samples synthesized in the reaction using PTFE are bluish black. The black color may be due to residual amorphous carbon in the samples, while the blue color indicates electron doping into the compounds; slightly electron doped niobium oxides, for example niobium blue bronze [19], indeed show blue color. Probably a small amount of oxygen or fluorine deficiency occurs during the synthesis. The amount must be very small, so that there is no difference in the lattice constants compared with those of the stoichiometric samples. On the other hand, it is noted that electron doped $Nb_2O_{5\text{-}x}F_x$ was not produced in this synthesis, which is in contrast to the reaction of WO_3 with PTFE, which produced heavily electron-doped superconductor $WO_{3\text{-}x}F_x$. Possibly, W^{6+} in $5d^0$ is more susceptible to electron doping than Nb^{5+} in $4d^0$.