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A B S T R A C T

Titanate pyrochlores are candidate host materials for the disposition of plutonium from dismantled nuclear weapons. These pyrochlores also -have potential applications as solid electrolytes and oxygen gas sensors. The radiation-induced microstructural evolution of titanate pyrochlores has been characterized using x-ray photoelectron spectroscopy (XPS). XPS analysis of the Ti 2p and 0 1s binding energy shifts of $A_2Ti_2O_7$ surface layers before and after irradiation shows that the primary manifestations of amorphization are distortions or changes in the coordination number of the titanium polyhedra. A model based on glass network structure was developed, and predictions of the relative susceptibilities for amorphization of the titanate pyrochlores are obtained that are consistent with the experimental results.

INTRODUCTION

Isometric pyrochlore (*Fd3m*), ideally $A_2B_2O_7$, is a derivative of the fluorite structure (AX_2), but with two cations and one-eighth of the oxygen ions absent. The A- and B-site cations are at equivalent positions, but there are two different types of oxygens. The first type of oxygen (48f) has two A-cation neighbors and two B-cation neighbors. The second type (8b) is on a tetrahedral site that consists entirely of A-cations. Pyrochlore is one of the candidate materials proposed for the immobilization of actinide-rich wastes, and it has recently been selected as a key component in Synroc-based pyrochlore-rich ceramics for the geological immobilization of surplus Pu in the USA [1]. A principal concern with crystalline waste forms is the possibility of radiation-induced amorphization due to the effects of a decay of the actinides [2]. The amorphization of pyrochlore as induced by ion irradiation is of interest because the process of amorphization represents a fundamental microstructural change, and an understanding of the underlying amorphization mechanism can be applied to the design of more radiation-tolerant materials [3]. In a previous study, we found that $Gd_2Ti_2O_7$ single crystals amorphized under 1.5 MeV Xe^+ ions at a fluence of 1.7 x 1 0^{14} Xe^+/cm^2. Cross-sectional transmission electron microscopy revealed a 300 nm-thick amorphous layer at the specimen surface. X-ray photoelectron spectroscopy (XPS) analysis of the Ti 2p and 0 1s electron binding energy shifts of $Gd_2Ti_2O_7$ before and after amorphization showed that the main results of ion-irradiation-induced disorder are a decrease in the coordination number of the titanium polyhedra and a transformation of the Gd-0 bond [4]. These features resemble those occurring in titanate glass formation. Here, we use XPS to study the microstructural changes of the other rare-earth titanate pyrochlores after ion irradiation, A model based on this glassy network structure is developed, and this model is used to predict the relative susceptibility to amorphization of the other titanate pyrochlores.

EXPERIMENTAL DETAILS

Ion-irradiation of the pyrochlore samples was carried out using the HVEM-Tandem Accelerator Facility at the Argonne National Laboratory. The samples (-2 mm in diameter) were irradiated by 1 .O MeV Kr^+ ions to an ion fluence of 1.7 x 10^{14} Xe^+/cm^2. XPS investigations were performed using an ESCA LAB5 XPS spectrometer with a Mg K_α x-ray source ($h\nu$ = 1253.6 eV). The samples were ultrasonically cleaned in acetone and ethanol for 5 minutes each, held in a high-vacuum chamber for at least 12 hours, and then mounted in the high-vacuum chamber of the XPS spectrometer where the vacuum was maintained at ~3.7×10^{-9} Torr. Ar^+ sputtering was used to remove carbon and surface contamination. The sputtering time was 3 minutes in order to control the etching depth to less than 10 nm. A carbon layer was deposited on the surface of the sample holder in order to calibrate the binding energy shifts resulting from surface charging effects.

RESULTS AND DISCUSSIONS

Due to the short inelastic mean free path (imfp) and sensitivity to chemical surroundings of the photoelectrons, XPS is used for the characterization of changes in the chemical environment of an element in a structure, especially in the case of amorphous materials. The imfp of a photoelectron is a function of its kinetic energy. The typical range of energies of the photoelectron is 100-l 000 eV; the imfp is on the order of 0.5~5 nm in oxides [5]. Figure 1 shows the XPS spectra of $Sm_2Ti_2O_7$ before and after 1 .O MeV Kr^+ ion irradiation. The Ti $2p_{3/2}$ binding energy increases from 458.2 eV to 459.6 eV and that of Ti $2p_{1/2}$ increases from 464.0 eV to 464.8 eV. The increase in binding energy of an element is a consequence of the decrease in the effective negative charge [6]. In the present case, the increase in binding energy of the Ti 2p electrons indicates a decrease in the average electron density on the titanium. This decrease in electron density can be achieved by increasing the bond length, which indicates an increase of the coordination number or a distortion of the titanium polyhedra. This is opposite to what was found in $Gd_2Ti_2O_7$ where the coordination number of the titanium polyhedra decreased after ion irradiation [4]. In the structural study of glasses in the alkali-TiO_2 binary system, Rao[7] and Saka et al [8] demonstrated that there are both four-coordinated and six-coordinated Ti^{4+} coexisting in the glasses by using infrared spectroscopy (IR), x-ray radial distribution (RAD), and Raman spectroscopy. With the decrease of electronegativity of the alkali ion, the fraction of six-coordinated Ti^{4+} decreased in going from Li_2O-TiO_2 to Cs_2O-TiO_2, and the glass forming ability increased. These results indicate the possibility of a different coordination of titanium polyhedra other than four. In fact, Farges [9] found fivefold coordinated titanium polyhedra are quite common in metamict zirconolite and titanites by using x-ray absorption near-edge structure (XANES) spectroscopy. These results enlarge the scope of a glass-former as defined by Zachariasen[1 0] in which he concluded that all or most oxides effectively serving as glass-formers should have a three or four coordination number. From the present work and other studies [7-9], one sees the dependence of the susceptibility to amorphization on the quenching rate, which indicates that a glass modifier can act as a glass former at higher quenching rates.

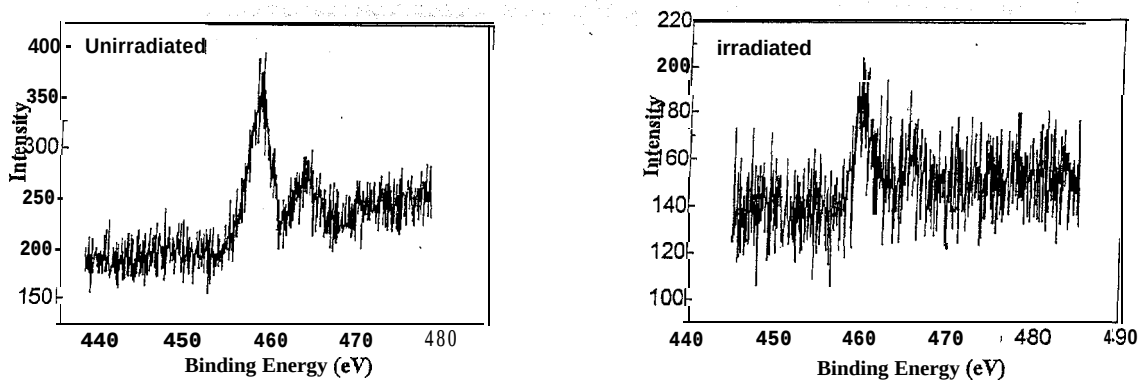

Figure 1. Ti 2p spectra of $Sm_2Ti_2O_7$ before and after ion irradiation

The binding energy of the 0 1s electrons changes from 529.6eV to 53 1.8eV(see figure 2) before and after ion irradiation. It can be seen that the shapes of the XPS

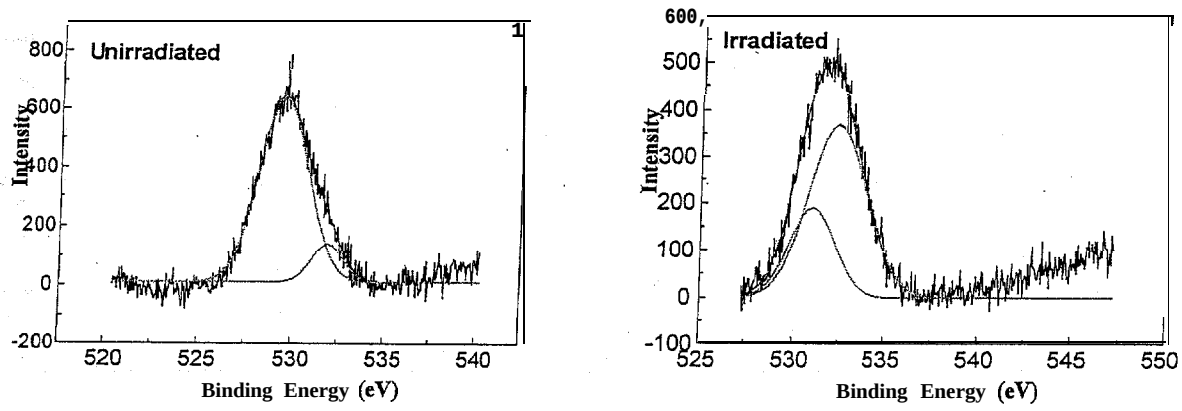

Figure 2. 0 1s spectra of $Sm_2Ti_2O_7$ before and after ion irradiation

spectra are not symmetric and can be fitted by two Gaussian functions. After ion irradiation, the two fitted Gaussian functions become more alike. This means that the chemical surroundings of the oxygen atoms are more similar. Since both the binding energy values of oxygen bonded to titanium and samarium increase after ion irradiation, either the coordination number changes or a distortion of the titanium and samarium polyhedra occurs. This is consistent with what was found in the Ti 2p XPS spectra. The binding-energy values of other titanate pyrochlores are shown in Table I.

It is not possible to form a bulk A_2O_3-TiO_2 glass by normal melting-quenching methods. In recent years, molecular dynamics (MD) simulations of the heavy particle irradiation of solids have shown that, after the initial collisional process, a region of atomic disorder in the collision cascade is created[1 l-1 3]. The disordered region within the collision cascade is sometimes viewed as a hot, transient, almost “liquid-like” zone. The energy within the cascade dissipates rapidly into the surrounding matrix in tens of pica-seconds. This quenching rate is much higher than that of normal glass formation methods. The structural changes

Table I Binding energy (BE) of some titanate pyrochlores

Compositions	Elements	BE (eV)/ unirradiated	BE (eV)/ irradiated
$Gd_2Ti_2O_7$	0 Is	526.1/531.2	528.0(527.4/529.6)*
	Ti 2p($2p_{3/2}/2p_{1/2}$)	459.4/465.2	458.4/464.3
	Gd 4p($4p_{3/2}$)	279.5	273.7
$Y_2Ti_2O_7$	0 Is	529.6(529.1/531.5)*	531.8(531.0/532.4)*
	Ti 2p($2p_{3/2}/2p_{1/2}$)	458.2/464.0	459.6/464.8
	Y 3d ($3d_{5/2}$)	158.0	160.0.
$Sm_2Ti_2O_7$	0 Is	529.6 (529.5/531.9)*	531.6 (531.0/532.3)*
	Ti 2p($2p_{3/2}/2p_{1/2}$)	458.0/463.5	460.2/465.7
	Sm 3 d($3d_{5/2}$)	1080.4	1083.2

*values in brackets are the binding energy of fitted Gaussian functions

before and after ion irradiation, indicated by the Ti 2p XPS results, show similarities between the ion-beam-induced amorphization of $A_2Ti_2O_7$ and the structural features produced by titanate glass formation.

The $A_2B_2O_7$ pyrochlore structure can be described in different ways. The most general description by Bystrom [14] is that the BO_6 octahedra link comer-to-corner to form a $[BO_6]$ network with A-cations filling the interstices. From the structural point of view and Zachariasen's glass network theory [1 0], such a structure has the elemental microstructure characteristics of a glass network. If the corner-to-comer sharing of the titanium polyhedra is maintained and reforms in a random network arrangement during or after ion irradiation, such a pyrochlore would be amorphized. Obviously, in the amorphization process, the rearrangements of oxygen have a significant effect on the amorphizatiori. Thus, we use the field strength difference term between the Ti^{4+} and A^{3+} ions in competing for oxygen atoms to evaluate the relative susceptibilities to amorphization of the titanate pyrochlores:

$$\Delta F = (Z_{Ti} / d^2_{Ti-O(48f)}) - (Z_A / d^2_{A-O(48f)}) \quad (1)$$

Here Z is the electrostatic charges of the cation and d is the cation-anion distance. In this calculation, we take into account the field strength difference between the Ti^{4+} and A^{3+} ions in competing for oxygen atoms at the 48f sites, because the oxygen atoms at the 8b sites make no contribution to the formation of the titanium polyhedral network. The calculated results are shown in Table IL The last column in this table shows the critical temperature (T_c) of the corresponding $A_2Ti_2O_7$ compound. The correlation between ΔF and T_c is good. When taking into account the melting temperature of $A_2Ti_2O_7$ as a kinetic factor for glass forming ability, the changing trend of corresponding term of $\Delta F/T_m^3$ correlates well with that of T_c (except for $Lu_2Ti_2O_7$). Taking $Gd_2Ti_2O_7$ as a reference, we can obtain the other titanate pyrochlores S values, which can be used as an empirical criterion of the $A_2Ti_2O_7$amorphization tendency.

The largest amorphization tendency shown by $Gd_2Ti_2O_7$ can also be explained from the smaller binding energy value of the 0 1 s electron. As shown in Table I, the 0 1 s value for $Gd_2Ti_2O_7$ before and after ion irradiation is smaller than those of the other titanate pyrochlores. This is not difficult to understanding considering the special atomic structure of gadolinium.

Gadolinium has one electron in the 5d orbital and two electrons in the 5s orbit with a half occupancy of the 4f

Table II ΦF and S of $A_2Ti_2O_7$ titanate pyrochlores

$A_2Ti_2O_7$	x	$d_{A-O(48f)}$ *	$d_{Ti-O(48f)}$ #	$T_m(K)$	ΦF	$\Phi F/T_m^3$ (_10^{11})	S	T_c (K)
$Sm_2Ti_2O_7$	0.327	2.53107	1.97311	2143.5	0.55915	5.682	0.87	1060
$Eu_2Ti_2O_7$	0.327	2.52192	1.96598	--	0.56322			1080
$Gd_2Ti_2O_7$	0.322	2.55508	1.94408	2093.5	0.59882	6.531	1	1100
$Y_2Ti_2O_7$	0.330	2.47585	1.95879	2173.5	0.553 10	5.530	0.85	780
$Er_2Ti_2O_7$	0.331	2.46691	1.96142	2253.5	0.54676	4.781	0.73	780
$Yb_2Ti_2O_7$	-	-		2203.5	-			620
$Dy_2Ti_2O_7$	0.323	2.5326	1.93628	2123.5	0.59918	6.262	0.96	-
$Lu_2Ti_2O_7$	0.330	2.45696	1.94385	2263.5	0.56164	4.846	0.74	480

*,# Calculation formulas are cited from reference[15]

orbital ($4f^7$) [16]. Gadolinium can easily give up its two electrons at the 5s orbital and one electron at the 5d orbital leading to a more ionic character of the of Gd-0 bond as compared with the other rare-earth elements (except Lu.) This results in the smallest 0 1s binding energy values in Table I. According to the glass-formation principle, the coexistence of ionic-type Gd-0 bonding and covalent Ti-0 bond in $Gd_2Ti_2O_7$ would be beneficial for the amorphization of $Gd_2Ti_2O_7$. The ionic character of the Gd-0 bond enables the titanium ion to bond to and "arrange" oxygen ions according its coordination requirements in a manner that is consistent with the observed ease of $Gd_2Ti_2O_7$ amorphization.

CONCLUSIONS

The XPS results for $Sm_2Ti_2O_7$ and $Y_2Ti_2O_7$ indicate possible distortions or changes in coordination number of the titanium polyhedra after ion irradiation. These results are opposite to what was found for $Gd_2Ti_2O_7$. Based on the field strength difference between titanium and rare-earth cation in competing for oxygen atoms at the 48f sites, an empirical model has been constructed, and the calculated and experimental results show a good correlation.

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