Synthesis, structure and dielectric properties of a new family of phases, ABC_3O_{11} : A = La, Pr, Nd, Sm, Gd; B = Zr, Hf; C = Ta, Nb

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Abstract

Eight new phases with the general formula of ABC_3O_{11} with different rare earth, (Zr, Hf), (Nb, Ta) combinations, have been prepared by solid-state reactions at a temperature range of 1200–1500 °C. The new phases—LaHfTa, LaHfNb, LaZrNb, PrHfTa, NdHfTa, NdHfNb, SmHfTa and GdHfTa—are characterised by X-ray and neutron diffraction data at room temperature and variable frequency impedance measurements. They are isostructural with $LaZrTa_3O_{11}$ which consist of alternating single layers of UO_7 pentagonal bipyramids and octahedra as shown by Rietveld refinement of X-ray and neutron powder diffraction data. Lattice parameters decrease with decreasing size of rare earth element substitution at A-site, and of all, Gd is the smallest rare earth that formed $LaZrTa_3O_{11}$ analogues. Detailed attempts of attained and unattainable $LaZrTa_3O_{11}$ analogues with different temperatures are included in this paper. All phases are highly insulating with temperature-independent bulk permittivities in the range 17 to 50; LaHfNb demonstrates the highest permittivity. Arrhenius plot shows that the activation energies are in the range 0.8 to 1.94 eV.

Keywords U_3O_7 pentagonal bipyramids · Rare earth · Low permittivity · Rietveld refinement

Introduction

The crystal structure of $LaZrTa_3O_{11}$ was first reported [1] in 1991 and was indexed on an orthorhombic unit cell, $a = 10.890(3)$ Å, $b = 12.450(3)$ Å and $c = 6.282(2)$ Å. However, its true symmetry was subsequently shown to be hexagonal with a geometrically related unit cell and space group $P6_322$ (no. 182) with $a = 6.2824(2)$ Å, $c = 12.4469$ Å and $Z = 2$ [2].

$LaZrTa_3O_{11}$ is isostructural with $CaTa_4O_{11}$ [3] which belongs to a series of compounds [4] with general formula

$Me_x(Nb,Ta)_{3n+1}O_{8n+3}$, e.g. $n = 1$: $CaTa_4O_{11}$, $Na_2Nb_4O_{11}$, $Na_2Ta_4O_{11}$, $K_2Ta_4O_{11}$, $Ag_2Nb_4O_{11}$, $Ag_2Ta_4O_{11}$ and “ $Cu_2Ta_4O_{11}$ ”; $n = 2$: $RETa_7O_{19}$ where $RE = La-Eu$, Y and Bi; intergrowth of 1 and 2: $Cu_5Ta_{11}O_{30}$. These phases are structurally related to $\alpha-U_3O_8$ whose structure exhibits layers of UO_7 pentagonal bipyramids sharing edges in the equatorial plane and apical oxygens [5]. These layers are repeated identically in the perpendicular direction. However, the $LaZrTa_3O_{11}$ structure has an alternating single layer of (Ta, Zr) O_7 pentagonal bipyramids with layers containing (Ta, Zr) O_6 octahedra and LaO_8 polyhedron; consecutive (Ta, Zr) O_7 layers are rotated by 180° relative to each other. La occupies an octahedral $2c$ site and a 3:1 disordered distribution of Ta and Zr occupy $6g$ pentagonal bipyramidal and $2d$ octahedral sites. Figure 1 illustrates the layers of pentagonal bipyramids alternating with octahedra. $LaZrTa_3O_{11}$ is highly insulating with electrical conductivity as low as $3 \times 10^{-7} \Omega^{-1} \text{ cm}^{-1}$ at 800 °C [1].

Given the ferroelectric and antiferroelectric nature of some structurally related materials [6–9], namely $Ag_2Nb_4O_{11}$, $Na_2Nb_4O_{11}$ and its solid solution $(Na_{1-x}Ag_x)Nb_4O_{11}$, it has been of interest to seek other members of this structural family and to evaluate their electrical properties. In this work, the synthesis of phases isostructural with $LaZrTa_3O_{11}$ with the

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Fig. 1 **a** Stacking sequence of single layers of pentagonal bipyramids alternate with single layers of octahedral layers and **b** layer of pentagonal bipyramids at $z = 0$

general formula of ABC_3O_{11} ; $A = La^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Gd^{3+}$, $B = Zr^{4+}, Hf^{4+}$ and $C = Ta^{5+}, Nb^{5+}$ is reported. Structure determination by Rietveld refinement of several of the new phases was determined using X-ray and neutron powder diffraction data. A preliminary measurement of their electrical properties was made using impedance spectroscopy.

Experimental

Starting materials were Ta_2O_5 , Nb_2O_5 , ZrO_2 , HfO_2 , La_2O_3 , Pr_6O_{11} , Nd_2O_3 (99.9% pure, Stanford Materials) and Sm_2O_3 , Gd_2O_3 (99.9% pure, Sigma-Aldrich). They were dried at 800–1000 °C and stored under vacuum. Mixtures totalling 3–5 g were weighed, mixed with acetone using an agate mortar and pestle, dried, pressed into pellets and fired in Pt crucibles in the air in electric muffle furnaces. The mixtures were heated at different times and temperatures in the range 1000–1500 °C for up to 3 days, intermittently. Pellets were removed from the furnace, crushed into a fine powder, repelleted and returned to the furnace. Reaction conditions were determined by trial and error, taking account of the refractory nature of the oxide reagents which meant that long period at high temperatures were required for the reaction to occur. Not any of the compositions are single-phase products (Table 1). The residual amounts of secondary phases remained, even after repeated firing. However, a relatively small amount of impurity is negligible for some compositions since they barely affect the results.

Phase analysis by X-ray powder diffraction (XRD) was carried out using a STOE Stadi P diffractometer, $CuK\alpha_1$ radiation ($\lambda = 1.54056 \text{ \AA}$). NIST 640d Si was used as an external standard for line position calibration. Data were processed and compared against reference data in the ICDD's PDF-2 database using the WinX^{POW} software package. Room temperature time-of-flight (ToF) neutron powder diffraction (ND) data were collected on the general material diffractometer

(GEM) at the ISIS facility, Rutherford Appleton Laboratory, RAL, Oxford, for $LaHfNb_3O_{11}$ powder in a vanadium can. Data were collected in the backscattering detector bank (50.07° – 74.71°), bank 4 with resolution $\Delta Q/Q \sim 0.79 \times 10^{-2}$. Rietveld refinement was performed using the EXPGUI interface for GSAS and both XRD and ND data.

For electrical measurements, cylindrical sintered pellets were coated with Pt paste electrodes on opposite faces and hardened by heating in the air at 800 °C for 2 h. The samples, with electrodes attached, were placed in a ceramic compression jig inside a furnace controlled and measured to ± 1 °C. Impedance spectroscopy (IS) measurements were performed using Hewlett Packard 4192A and Solartron 1260/1286 impedance analysers at frequencies 10 Hz–1 MHz and 1 kHz–1 MHz, respectively. Impedance data were recorded between room temperature and 800 °C in the air with 100-mV applied *ac* voltage. Data were corrected for overall pellet geometry and for the blank cell capacitance (jig correction) and analysed using the software program ZView.

Results and discussion

Reaction conditions and products

Results of the attempted synthesis of new phases with different rare earth, Zr, Hf/Nb, and Ta combinations are summarised in Table 1. Eight new phases, in addition to $LaZrTa_3O_{11}$, were prepared, and for each, the synthesis conditions are detailed. Attempted synthesis of a further 12 new phases was unsuccessful; details of the reaction conditions and products, in which there was no evidence of formation of a phase with the $LaZrTa_3O_{11}$ structure, are given in Table 1(b).

The new phases were readily recognised by the similarity of their XRD patterns to that of $LaZrTa_3O_{11}$.

Powder XRD patterns of these new phases are shown in Figs. 2 and 3 for the Ta-based and Nb-based compositions,

Table 1 Results of heat treatment on different ABC_3O_{11} combinations: (a) those which yielded an $LaZrTa_3O_{11}$ analogue, (b) those for which an $LaZrTa_3O_{11}$ analogue was not obtained

No.	Compositions	T (°C)	Time (h)	Phases present
(a)				
1.	$LaZrTa_3O_{11}$ (LZT)	1500	12	LZT, $LaTa_3O_9$, ZrO_2
		1500	24	LZT, $LaTa_3O_9$, ZrO_2
		1500	36	LZT, $LaTa_3O_9$, ZrO_2
		1500	48	LZT, $LaTa_3O_9$, ZrO_2
		1500	72	LZT, trace of $LaTa_3O_9$ and ZrO_2
2.	$LaHfTa_3O_{11}$ (LHT)	1500	24	LHT, HfO_2
		1500	48	LHT, trace of HfO_2
3.	$LaHfNb_3O_{11}$ (LHN)	1150	24	LHN, Nb_2O_5 , La_2O_3 , HfO_2
		1250	36	LHN, Nb_2O_5 , La_2O_3 , HfO_2
		1300	96	LHN, trace of HfO_2
		1350	108	Melt
4.	$LaZrNb_3O_{11}$ (LZN)	1000	12	$La_2Zr_2O_7$, LZN, Nb_2O_5 , La_2O_3 , ZrO_2
		1150	36	LZN, $LaNb_3O_9$, La_2O_3 , ZrO_2
		1150	48	$LaNb_3O_9$, LZN, La_2O_3 , ZrO_2
		1200	60	$LaNb_3O_9$, $Nb_2Zr_6O_{17}$
5.	$PrHfTa_3O_{11}$ (PHT)	1350	54	PHT, Ta_2O_5 , HfO_2
		1500	78	PHT, Ta_2O_5 , HfO_2
		1500	102	PHT, Ta_2O_5 , HfO_2
		1500	126	PHT, HfO_2
		1500	150	PHT, trace of HfO_2
6.	$NdHfTa_3O_{11}$ (NHT)	1000	12	Ta_2O_5 , $NdTa_7O_{19}$, HfO_2
		1500	24	NHT, Ta_2O_5 , HfO_2
		1500	48	NHT, Ta_2O_5 , HfO_2
		1500	60	NHT, trace of Ta_2O_5 and HfO_2
7.	$NdHfNb_3O_{11}$ (NHN)	1000	24	$NdNbO_4$, Nb_2O_5 , HfO_2 , Nd_2O_3
		1100	36	$NdNbO_4$, Nb_2O_5 , HfO_2 , Nd_2O_3
		1150	72	NHN, $NdNb_3O_9$, HfO_2 , Nd_2O_3
		1200	96	$NdNb_3O_9$, NHN, HfO_2 , Nd_2O_3
		1250	108	$NdNb_3O_9$, HfO_2 , Nd_2O_3
8.	$SmHfTa_3O_{11}$ (SHT)	1200	12	SHT, $SmTa_3O_9$, Ta_2O_5 , HfO_2 , Sm_2O_3
		1300	24	SHT, $SmTa_3O_9$, Ta_2O_5 , HfO_2 , Sm_2O_3
		1350	72	SHT, $SmTa_3O_9$, Ta_2O_5 , HfO_2
		1375	84	SHT, $SmTa_3O_9$, Ta_2O_5 , HfO_2
		1400	96	SHT, $SmTa_3O_9$, Ta_2O_5 , HfO_2
		1500	108	$SmTa_3O_9$, SHT, HfO_2
		1500	108	GHT, $GdTa_3O_9$, Ta_2O_5 , HfO_2 , Gd_2O_3
9.	$GdHfTa_3O_{11}$ (GHT)	1200	12	GHT, $GdTa_3O_9$, Ta_2O_5 , HfO_2 , Gd_2O_3
		1300	24	GHT, $GdTa_3O_9$, Ta_2O_5 , HfO_2 , Gd_2O_3
		1350	72	GHT, $GdTa_3O_9$, Ta_2O_5 , HfO_2
		1375	84	GHT, $GdTa_3O_9$, Ta_2O_5 , HfO_2
		1400	96	GHT, $GdTa_3O_9$, Ta_2O_5 , HfO_2
		1500	108	$GdTa_3O_9$, LZT, HfO_2

Table 1 (continued)

No.	Compositions	T (°C)	Time (h)	Phases present
(b)				
1.	$DyHfTa_3O_{11}$	1000	12	Unknown, $DyTaO_4$, Ta_2O_5 , Dy_2O_3 , HfO_2
		1300	120	Unknown, $DyTaO_4$, Ta_2O_5 , Dy_2O_3 , HfO_2
2.	$ErHfTa_3O_{11}$	1000	12	Ta_2O_5 , Er_2O_3 , HfO_2
		1150	36	$ErTaO_4$, Ta_2O_5 , Er_2O_3 , HfO_2
		1200	60	$ErTaO_4$, Ta_2O_5 , Er_2O_3 , HfO_2
		1250	72	$ErTa_7O_{19}$, $ErTaO_4$, Ta_2O_5 , HfO_2
3.	$PrHfNb_3O_{11}$	1000	15	$PrNbO_4$, Nb_2O_5 , HfO_2 , Pr_6O_{11}
		1100	40	$PrNb_5O_{14}$, $PrNb_3O_9$, Nb_2O_5 , HfO_2
		1150	60	$PrNb_5O_{14}$, $PrNb_3O_9$, HfO_2
		1300	72	$PrNb_5O_{14}$, $PrNb_3O_9$, HfO_2
4.	$PrZrTa_3O_{11}$	1350	54	$Ta_4Zr_{11}O_{32}$, ZrO_2 , Ta_2O_5
5.	$PrZrNb_3O_{11}$	1000	15	$PrNbO_4$, Nb_2O_5 , HfO_2 , Pr_6O_{11}
		1100	41	$PrNb_5O_{14}$, $PrNb_3O_9$, ZrO_2
		1300	53	$PrNb_5O_{14}$, $PrNb_3O_9$, ZrO_2
6.	$NdZrTa_3O_{11}$	1500	72	$NdTa_3O_9$, $Ta_4Zr_{11}O_{32}$, ZrO_2
7.	$NdZrNb_3O_{11}$	1000	24	$NdNbO_4$, Nb_2O_5 , ZrO_2 , Nd_2O_3
		1050	36	$NdNbO_4$, Nb_2O_5 , ZrO_2 , Nd_2O_3
		1150	48	$NdNb_5O_{14}$, Nb_2O_5 , ZrO_2 , Nd_2O_3
8.	$SmZrNb_3O_{11}$	1000	24	Nb_2O_5 , ZrO_2 , Sm_2O_3
		1050	36	Nb_2O_5 , ZrO_2 , Sm_2O_3
		1150	48	Nb_2O_5 , ZrO_2 , Sm_2O_3
9.	$SmHfNb_3O_{11}$	1000	24	Nb_2O_5 , HfO_2 , Sm_2O_3
		1100	36	$SmNbO_4$, Nb_2O_5 , HfO_2
		1200	60	$SmNbO_4$, Nb_2O_5 , HfO_2
10.	$GdHfNb_3O_{11}$	1000	24	$GdNbO_4$, Nb_2O_5 , HfO_2 , Gd_2O_3
		1050	36	$GdNbO_4$, Nb_2O_5 , HfO_2 , Gd_2O_3
		1150	48	$GdNbO_4$, Nb_2O_5 , HfO_2 , Gd_2O_3
11.	$GdZrNb_3O_{11}$	1000	24	$GdNbO_4$, Nb_2O_5 , ZrO_2 , Gd_2O_3
		1050	36	$GdNbO_4$, Nb_2O_5 , ZrO_2 , Gd_2O_3
		1150	48	$GdNbO_4$, Nb_2O_5 , ZrO_2 , Gd_2O_3
12.	$YbZrTa_3O_{11}$	1500	72	Ta_2O_5 , Yb_2O_3 , ZrO_2

respectively. Indexed data for one analogue, $LaHfTa_3O_{11}$, are given in Table 2; data for all the analogues have been submitted for inclusion in the ICDD powder diffraction file. Unit cell data are summarised in Table 3.

The lattice parameters decreased on the substitution of La by smaller rare earth elements. Gd was the smallest rare earth that formed $LaZrTa_3O_{11}$ analogue. With three cationic components in each phase, rare earth, Zr/Hf and Nb/Ta, there is a complex interplay between ion size, possible formation of $LaZrTa_3O_{11}$ analogue and its thermal stability. It was found

Fig. 2 XRD profiles of $\text{AHfTa}_3\text{O}_{11}$ compositions. Asterisks indicate unreacted HfO_2 , triangles indicate unreacted Ta_2O_5 and circles indicate ATa_3O_9

that a standard set of synthesis conditions could not be used for all the new phases. In general, higher reaction temperatures ($\sim 1500^\circ\text{C}$) were required to obtain Ta-based phases compared to the reaction temperatures needed for the Nb analogues ($1200\text{--}1300^\circ\text{C}$), consistent with the lower reactivity of Ta_2O_5 compared to Nb_2O_5 . However, fewer Nb-based family members were prepared successfully, and those that did form had less thermal stability than the Ta analogues and decomposed at above $\sim 1400^\circ\text{C}$.

For Ta-based phases, $\text{LaHfTa}_3\text{O}_{11}$ was the easiest to prepare and obtain as a phase with $\text{LaZrTa}_3\text{O}_{11}$ structure, whereas the smaller rare earths require increasingly longer reaction times and lower temperatures. $\text{SmHfTa}_3\text{O}_{11}$ and $\text{GdHfTa}_3\text{O}_{11}$ started to form at 1200°C , as shown by the

traces of $\text{LaZrTa}_3\text{O}_{11}$ patterns in the XRD data. The impurity phases remained similar until 1400°C , and although peak intensities decreased with time, Sm and Gd target phases were still not phase-pure and decomposed after increasing the temperature to 1500°C .

In the niobate systems, only three compositions produced $\text{LaZrTa}_3\text{O}_{11}$ analogues: $\text{LaHfNb}_3\text{O}_{11}$, $\text{LaZrNb}_3\text{O}_{11}$ and $\text{NdHfNb}_3\text{O}_{11}$, which are all formed at temperatures in the range $1150\text{--}1300^\circ\text{C}$. These niobates have lower thermal stability than their corresponding tantalates. $\text{LaHfNb}_3\text{O}_{11}$ has an upper limit of stability at 1300°C before melting at 1350°C , $\text{NdHfNb}_3\text{O}_{11}$ appears to have an upper limit of stability at $\sim 1200^\circ\text{C}$ and $\text{LaZrNb}_3\text{O}_{11}$ appears to be on the edge of stability at 1150°C . The presence of $\text{LaZrTa}_3\text{O}_{11}$ phase was

Fig. 3 XRD profiles of $\text{ABNb}_3\text{O}_{11}$ compositions, LHN contains unreacted HfO_2 (asterisk), whereas LZN and NHN are mixed phases

Table 2 X-ray powder diffraction data for LaHfTa₃O₁₁

$2\theta(\text{obs})$	$h\ k\ l$	$2\theta(\text{calc})$	Obs– calc	<i>Int.</i>	$d\ (\text{obs})\ \text{\AA}$	$d\ (\text{calc})\ \text{\AA}$
14.240	0 0 2	14.229	0.0108	31.0	6.2149	6.2196
16.280	1 0 0	16.287	−0.0066	49.0	5.4402	5.4380
17.797	1 0 1	17.787	0.0106	6.6	4.9798	4.9827
21.709	1 0 2	21.691	0.0187	19.8	4.0904	4.0939
27.050	1 0 3	27.020	0.0296	4.0	3.2937	3.2973
28.728	0 0 4	28.683	0.0454	57.0	3.1050	3.1098
29.328	1 1 1	29.315	0.0131	89.6	3.0428	3.0442
31.910	1 1 2	31.904	0.0054	100.0	2.8023	2.8028
33.170	1 0 4	33.159	0.0119	12.2	2.6986	2.6996
35.868	1 1 3	35.847	0.0217	31.8	2.5016	2.5030
39.613	2 0 3	39.605	0.0076	2.1	2.2733	2.2737
40.819	1 1 4	40.808	0.0103	2.9	2.2089	2.2094
43.638	0 0 6	43.622	0.0157	4.8	2.0725	2.0732
44.029	2 1 0	44.021	0.0085	6.2	2.0550	2.0554
44.647	2 1 1	44.649	−0.0018	8.4	2.0280	2.0279
46.549	1 1 5	46.538	0.0113	27.5	1.9494	1.9499
46.879	1 0 6	46.861	0.0185	3.1	1.9365	1.9372
49.459	2 1 3	49.453	0.0055	4.2	1.8413	1.8415
50.299	3 0 0	50.295	0.0034	32.8	1.8126	1.8127
52.549	3 0 2	52.544	0.0051	4.9	1.7401	1.7403
52.880	1 1 6	52.878	0.0015	31.0	1.7300	1.7301
53.389	2 1 4	53.389	−0.0000	6.3	1.7147	1.7147
55.728	2 0 6	55.710	0.0181	6.5	1.6481	1.6436
58.174	2 1 5	58.173	0.0016	4.0	1.5845	1.5846
58.938	3 0 4	58.928	0.0104	35.6	1.5658	1.5651
59.299	2 2 1	59.285	0.0140	11.6	1.5571	1.5575
59.749	1 1 7	59.747	0.0016	13.4	1.5455	1.5455
60.799	2 2 2	60.806	−0.0076	14.1	1.5223	1.5221
61.400	3 1 0	61.425	−0.0245	5.1	1.5038	1.5032
61.964	3 1 1	61.924	0.0399	4.1	1.4954	1.4973
63.289	2 2 3	63.294	−0.0046	7.9	1.4632	1.4631
63.709	2 1 6	63.705	0.0043	3.1	1.4595	1.4596
65.869	3 1 3	65.840	0.0294	2.1	1.4168	1.4174
68.749	3 0 6	68.732	0.0174	2.7	1.3643	1.3646
69.168	3 1 4	69.170	−0.0013	5.0	1.3571	1.3571
69.928	2 1 7	69.922	0.0060	2.8	1.3442	1.3443
70.932	4 0 2	70.898	0.0332	6.0	1.3276	1.3281
73.344	3 1 5	73.347	−0.0023	2.2	1.2898	1.2897
75.020	1 1 9	75.025	−0.0054	4.9	1.2651	1.2650
75.979	2 2 6	75.975	0.0039	8.8	1.2515	1.2515
76.369	4 0 4	76.396	−0.0269	2.6	1.2450	1.2457
76.790	2 1 8	76.806	−0.0153	2.8	1.2403	1.2400
78.050	3 2 2	78.062	−0.0120	4.4	1.2234	1.2232
78.889	1 0 10	78.876	0.0132	1.8	1.2124	1.2126

Crystal symmetry: hexagonal

Refined cell: $a = 6.28319(6)\ \text{\AA}$, $\alpha = 90.0^\circ$, ($a = b$), $c = 12.4358(2)\ \text{\AA}$, $\gamma = 120.0^\circ$, $V = 425.173(8)\ \text{\AA}^3$ **Table 3** Lattice parameters and unit cell volumes for ABC₃O₁₁ phases

No.	Phases	Observed unit cell parameters ($\text{\AA}$)		Volume ($\text{\AA}^3$)
		<i>A</i>	<i>c</i>	
1.	LaZrTa ₃ O ₁₁ (LZT)	6.28724(4)	12.4525(1)	426.296(5)
2.	LaHfNb ₃ O ₁₁ (LHN)	6.2986(2)	12.4189(5)	426.68(3)
3.	LaHfTa ₃ O ₁₁ (LHT)	6.28319(6)	12.4358(2)	425.173(8)
4.	PrHfTa ₃ O ₁₁ (PHT)	6.281145(8)	12.4412(2)	425.08(3)
5.	NdHfTa ₃ O ₁₁ (NHT)	6.2578(1)	12.3938(3)	420.32(2)
6.	SmHfTa ₃ O ₁₁ (SHT)	6.23885(8)	12.3569(2)	416.53(1)
7.	GdHfTa ₃ O ₁₁ (GHT)	6.2293(1)	12.3421(3)	414.77(2)

Fig. 4 The observed (+), calculated (—) and difference (—) profiles from Rietveld refinement of $\text{LaHfTa}_3\text{O}_{11}$ with a disordered arrangement of Ta, Hf in the ratio 3:1. Ticks marks represent Bragg peak positions

detected after ~ 36 h but decomposed to LaNb_3O_9 after another 12 h of reaction time.

Structure refinements

Rietveld refinement using XRD data was carried out for three compositions: $\text{LaHfTa}_3\text{O}_{11}$, $\text{PrHfTa}_3\text{O}_{11}$ and $\text{NdHfTa}_3\text{O}_{11}$. For the fourth composition, $\text{LaHfNb}_3\text{O}_{11}$, combined refinement using XRD and ND data was conducted. For each refinement, the crystal structure of $\text{LaZrTa}_3\text{O}_{11}$ was used as the starting model with La on octahedral $2c$ sites, Ta and Hf

disordered in a fixed 1:3 ratio on octahedral $6g$ and $2d$ sites and oxygen on $4f$, $6g$ and $12i$ sites. Total occupancies for all sites were fixed at unity; background and peak profile parameters were refined first using the Chebyshev function with ten terms for the background. This was followed by the single positional variable for the $6g$ site and simultaneous refinement of the isotropic thermal parameters, U_{iso} , of the cation sites until convergence, with negligible shifts in atomic variables.

The statistical measures and visual fits shown in Figs. 4, 5, 6 and 7 were relatively good. For $\text{LaHfTa}_3\text{O}_{11}$, $\chi^2 = 4.704$, R factors $< 7\%$ and thermal, or U_{iso} , parameters were all refined to acceptable, positive values. For $\text{PrHfTa}_3\text{O}_{11}$ and

Fig. 5 The observed (+), calculated (—) and difference (—) profiles from Rietveld refinement of $\text{PrHfTa}_3\text{O}_{11}$ with disordered arrangement of Ta, Hf in the ratio 3:1. Ticks marks represent Bragg peak positions

Fig. 6 The observed (+), calculated (–) and difference (–) profiles from Rietveld refinement of $\text{NdHfTa}_3\text{O}_{11}$ with disordered arrangement of Ta, Hf in the ratio 3:1. Ticks marks represent Bragg peak positions

$\text{NdHfTa}_3\text{O}_{11}$, good fits were also obtained with acceptable statistical measures. U_{iso} values were positive for all atoms, indicating that the statistical occupancies of Ta, Hf over both sites is reasonable; with the χ^2 value for $\text{PrHfTa}_3\text{O}_{11}$ at 7.475 compared to 5.996 for $\text{NdHfTa}_3\text{O}_{11}$. The final atomic coordinates and bond distances are presented in Tables 4 and 5. The unreacted HfO_2 peak in $\text{LaHfTa}_3\text{O}_{11}$ and $\text{PrHfTa}_3\text{O}_{11}$ was so small that it could barely affect the refinements with the weight fraction 0.165 and 0.047%, respectively. As for $\text{NdHfTa}_3\text{O}_{11}$, impurities of NdTa_3O_9 and unreacted HfO_2 are taken into account with weight fraction 1.236 and 0.774%,

respectively, with the lattice parameters obtained for NdTa_3O_9 : $a = 3.9127(9) \text{ \AA}$, $c = 7.865(3) \text{ \AA}$.

For $\text{LaHfNb}_3\text{O}_{11}$, the ToF ND data were collected at room temperature. The background, diffractometer constant DIFA and peak profiles were refined for the ToF histogram with fixed values of lattice parameters and unit cell volume, which were then refined together with atomic positions and U_{iso} , with initial values of $0.005 \text{ \AA}^2$. The whole process was repeated until convergence. Combined structure refinement gave a good visual fit and statistical measures (Fig. 7, Table 4), although χ^2 was inconsiderably high, 5.878.

Fig. 7 Observed (+), calculated (–) and difference (–) ND profiles at room temperature using constant wavelength ND data of $\text{LaHfNb}_3\text{O}_{11}$. Tick marks represent Bragg peak positions

Table 4 Structural refinement data for LaHfTa₃O₁₁, PrHfTa₃O₁₁, NdHfTa₃O₁₁ and LaHfNb₃O₁₁

Sites	Properties	LaHfTa ₃ O ₁₁	PrHfTa ₃ O ₁₁	NdHfTa ₃ O ₁₁	LaHfNb ₃ O ₁₁
2c (RE elements)	(x, y, z)	0.3333, 0.6667, 0.25	0.3333, 0.6667, 0.25	0.3333, 0.6667, 0.25	0.3333, 0.6667, 0.25
	<i>U</i> _{iso}	0.3(2)	0.7(2)	0.3(3)	0.50(4)
	Occupancy	1.0	1.0	1.0	1.0
6g (Ta, Hf/Nb)1	(x, y, z)	0.6418(2), 0.0, 0.0	0.6414(2), 0.0, 0.0	0.6413(2), 0.0, 0.0	0.6430(1), 0.0, 0.0
	<i>U</i> _{iso}	0.50(3)	0.61(5)	0.50(5)	0.15(2)
	Occupancy	0.75 / 0.25	0.75 / 0.25	0.75 / 0.25	0.75 / 0.25
2d (Ta, Hf / Nb)2	(x, y, z)	0.3333, 0.6667, 0.75	0.3333, 0.6667, 0.75	0.3333, 0.6667, 0.75	0.3333, 0.6667, 0.75
	<i>U</i> _{iso}	0.5(1)	0.2(2)	0.3(2)	0.1(4)
	Occupancy	0.75 / 0.25	0.75 / 0.25	0.75 / 0.25	0.75 / 0.25
4f (O1)	(x, y, z)	0.3333, 0.6667, 0.39(1)	0.3333, 0.6667, 0.0042(2)	0.3333, 0.6667, 0.043(2)	0.3333, 0.6667, 0.388(1)
	<i>U</i> _{iso}	0.5(2)	0.8(3)	1.7(3)	0.38(3)
	Occupancy	1.0	1.0	1.0	1.0
6g (O2)	(x, y, z)	0.244(2), 0.0, 0.0	0.241(2), 0.0, 0.0	0.244(2), 0.0, 0.0	0.2484(2), 0.0, 0.0
	<i>U</i> _{iso}	0.5(2)	0.8(3)	1.7(3)	0.88(3)
	Occupancy	1.0	1.0	1.0	1.0
12i (O3)	(x, y, z)	0.949(2), 0.377(2), 0.3415(6)	0.953(3), 0.382(3), 0.3430(8)	0.953(3), 0.385(3), 0.3420(8)	0.944(1), 0.373(2), 0.34257(6)
	<i>U</i> _{iso}	0.5(2)	0.8(3)	1.7(3)	0.46(2)
	Occupancy	1.0	1.0	1.0	1.0
<i>a</i> (Å)		6.28320(6)	6.281145(8)	6.2578(1)	6.2986(2)
<i>c</i> (Å)		12.4358(2)	12.4412(2)	12.3939(3)	12.4189(5)
Cell volume, <i>V</i> (Å ³)		425.175(8)	425.08(1)	420.32(1)	426.68(3)
<i>R</i> _{wp} (%)		7.02	7.60	6.42	5.73
<i>R</i> _p (%)		5.30	5.74	4.389	4.46
χ ²		4.704	7.475	5.996	5.878

These new phases are isostructural with LaZrTa₃O₁₁ which contains two layers of pentagonal bipyramids related by the 6₃ symmetry axis sharing edges. Both octahedral layers, i.e. (Ta/Nb, Hf/Zr)(1)O₇ and (Ta/Nb, Hf/Zr)(2)O₆ contain a disordered 3:1 ratio of Ta/Nb and Hf/Zr, where (Ta/Nb, Hf/Zr)(1)O₇ at *z* = 0 and ½ corner-share four of their oxygens, O(1) and O(2) with each other and have two apical oxygens, O(3) along the *z*-axis. Meanwhile, (Ta/Nb, Hf/Zr)-O₆ and REO₆ octahedra that are located at *z* = ¼ and ¾ are formed

by the apical oxygens; three in the layer below and above (Ta/Nb, Hf/Zr)(1)-O₇ octahedra.

Electrical properties

Impedance measurements for several of the new phases over the range from room temperature to 800 °C showed that are all excellent insulators. The permittivities of ABC₃O₁₁ are in the range 17 ≤ ε' ≤ 50 and are essentially frequency-independent

Table 5 Selected bond distances of LaHfTa₃O₁₁, PrHfTa₃O₁₁, NdHfTa₃O₁₁ and LaHfNb₃O₁₁

Bonding		No.	LaHfTa ₃ O ₁₁ (Å)	PrHfTa ₃ O ₁₁ (Å)	NdHfTa ₃ O ₁₁ (Å)	LaHfNb ₃ O ₁₁ (Å)
(Ta, Hf/Nb)1	O1	2×	2.080(4)	2.087(5)	2.082(5)	2.0858(5)
	O2	2×	1.992(2)	1.988(3)	1.986(3)	1.9963(7)
	O3	2×	2.009(7)	1.992(9)	1.998(9)	1.9979(8)
	O2	1×	2.494(9)	2.51(1)	2.48(1)	2.485(2)
(Ta, Hf/Nb)2	O3	6×	2.012(9)	2.02(1)	2.01(1)	2.0014(7)
RE elements	O1	6×	2.61(2)	2.44(2)	2.56(2)	2.622(1)
	O3	2×	2.45(1)	2.58(2)	2.42(1)	2.4921(8)

Fig. 8 Permittivity, ϵ' , at room temperature for ABC_3O_{11} phases

over the range 10^4 to 10^7 Hz (Fig. 8). The highest permittivity is shown by $\text{LaHfNb}_3\text{O}_{11}$, ~ 50 , whilst the lowest is $\text{SmHfTa}_3\text{O}_{11}$, ~ 17 . The capacitance data of the tantalates from room temperature to 400°C were independent of frequency and temperature. The conductivity of all the samples was too low to measure at room temperature with the available instrumentation, indicative of highly insulating materials with $R \gg 10^9 \Omega\text{cm}$. At higher temperatures, the conductivity data were obtained from IS measurements and are shown as Arrhenius plots in Fig. 9. The highest conductivity was found for $\text{LaHfNb}_3\text{O}_{11}$, $\sim 10^{-5} \Omega^{-1}\text{cm}^{-1}$ at 1000 K. The activation energy, E_a , for conduction obtained from the gradient of the Arrhenius plots was in the range 0.8 and 1.94 eV.

Figure 10 shows the bulk permittivity, ϵ_∞ , of the tantalate phases at room temperature plotted against ionic radii of rare earth elements. The bulk permittivity decreased with

decreasing ionic radius; replacing Ta^{5+} by Nb^{5+} in one case increased the permittivity significantly.

Conclusions

A new family of phases based on $\text{LaZrTa}_3\text{O}_{11}$ with the general formula of ABC_3O_{11} : A = La, Pr, Nd, Sm; B = Zr, Hf and C = Ta, Nb, but not all combinations, has been prepared by solid-state reaction. The successful element combinations are LaHfTa , LaHfNb , LaZrNb , PrHfTa , NdHfTa , NdHfNb , NdZrNb , SmHfTa and GdHfTa . However, none were completely in phase pure as ATa_3O_9 and unreacted raw materials were often present. Similar to $\text{LaZrTa}_3\text{O}_{11}$, all new phases were indexed on the hexagonal space group $P6_322$;

Fig. 9 Conductivity data for the new phases **Fig. 10** Bulk permittivity of the tantalate phases at room temperature vs. ionic radii of rare earth elements

unit cell parameters and cell volume decreased with decreasing size of A.

The temperatures necessary for the sample synthesis depend on the size of A and C. Most AHfTa combinations were prepared at 1500 °C except for SmHfTa and GdHfTa which were prepared at 1400 °C and decomposed at 1500 °C. AHfNb₃O₁₁ compounds were prepared at 1150–1300 °C, which was significantly lower than required to synthesise the tantalates. With smaller rare earth ions, it was generally found to be increasingly difficult to eliminate secondary phases. Gd appears to be the smallest rare earth that allows formation of LaZrTa₃O₁₁ analogue phases.

The crystal structures have been confirmed by Rietveld refinement using both XRD and NPD data in space group *P*6₃22. All four structures that were refined contain a random distribution of (Ta, Nb) and Hf in the ration 3:1 over the two sites of edge-sharing octahedra.

All samples were insulating at room temperature and higher temperatures were required to obtain conductivity data. The activation energies are in the range 0.8–1.74 eV, consistent with the insulating nature of the materials. The capacitances of all the samples, in the form of sintered pellets, are frequency-independent at low temperatures and gradually increased as the temperature increased. Of all the samples, LaHfNb₃O₁₁ exhibits the highest permittivity ~50. There was no evidence of any ferroic transitions, but it would be interesting to measure the low temperature electrical properties of LaHfNb₃O₁₁.

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