BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 52 (2), 621—622 (1979)

Flux Growth of Double Oxide Crystals of Tantalum and Rare-earth Elements

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(Received July 5, 1978)

Synopsis. Crystals of $GdTaO_4$, $DyTaO_4$, and $ErTaO_4$, and those of Gd_3TaO_7, Y_3TaO_7, and Er_3TaO_7 have been grown by PbF_2–PbO flux. Solid solution crystals of $YTaO_4$ and $YNbO_4$ have been obtained for the starting composition of $YTa_xNb_{1-x}O_4 (x<0.5)$.

Niobium and tantalum occur in nature as fergusonite $Y(Nb,Ta)O_4$, columbite $(Fe,Mn)(Nb,Ta)_2O_6$, and samarskite $Y_4[(Nb,Ta)_2O_7]_3$, *etc.*[1] It is common for these minerals to contain radioactive elements such as U and Th as minor elements, so that they are in most cases in the 'metamict' form, giving an X-ray pattern like that of an amorphous phase. It is generally known that in inorganic compounds solid solutions are formed at any atomic ratio for Nb and Ta, and that with an increase in Ta content, the melting point of the compound increases, abruptly over 2000 °C.

The flux growth of fergusonite type crystals[2,3] $LnNbO_4$, where Ln is a rare-earth element has been reported, as have the new compounds of Ln_3NbO_7, the columbite type crystals of MNb_2O_6 and MTa_2O_6, where M is divalent transition metal. Although these compounds have high melting points, growth at temperatures below about 1300 °C has been achieved. In this paper the flux growth of the double oxides of rare-earth elements and tantalum at temperatures below 1500 °C are reported. Above 1500 °C the Pt crucible is seriously damaged.

As a typical case, the growing method of $GdTaO_4$ is given here. Other compounds can be grown, in general, in a manner similar to that for $GdTaO_4$, with some minor changes in the conditions such as the composition of the starting materials, solute-flux ratio, *etc.* Reagents of Ln_2O_3 (purity 4N) and Ta_2O_5 (purity 4N) were used for the growth experiment. As flux materials, PbF_2–PbO, Bi_2O_3–V_2O_5, and B_2O_3–$Na_2B_4O_7$ were used at various flux ratios. The purity of PbF_2 and PbO was 3N, and the others were of chemical reagent grade.

A mixture of the starting material (Gd_2O_3 5 mM+Ta_2O_5 5 mM) was put into a 20 ml platinum crucible together with the flux material (PbF_2 40 mM+PbO 10 mM), and tightly covered with a platinum lid. The crucible was placed in an electric muffle furnace kept at 1350 °C for 10 h. Cooling to 900 °C was achieved at the rate of 1—3 °C/h, program controlled. At the final temperature the crucible was taken from the furnace and air quenched to room temperature. The products obtained were washed with hot dilute HNO_3 for several hours. The crystals thus obtained were identified as the desired materials by X-ray powder diffraction.

Figure 1 shows the crystals of $GdTaO_4$ obtained by using PbF_2–PbO flux. The regular crystals are octahedral in shape, ranging in size from 0.5—2.5 mm in the longest directions.

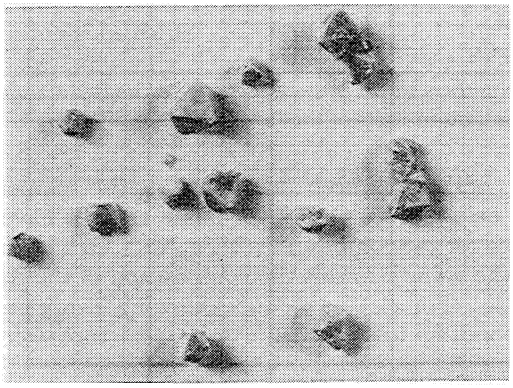

Fig. 1. Crystals of $GdTaO_4$ (1 division=1 mm).

Of the flux materials tried, only the PbF_2–PbO system was suitable for the growth of Ln–Ta–O system compounds. A list of crystals obtained from the PbF_2–PbO flux is given in Table 1, where the compounds presented in each row were obtained from the same melt. Crystals having $LnTaO_4$ composition are those with Ln=Gd, Dy, and Er. They were found to be monoclinic and isostructural with $LnNbO_4$ with a fergusonite structure, the cell parameters of which are given in Table 2. Attempts at growing other $LnTaO_4$ type compounds at higher temperatures (*i.e.* up to about 1500 °C) were not successful. Compounds of Gd_3TaO_7, Y_3TaO_7, and Er_3TaO_7 belong to the cubic system, and have been related to the Ln_3NbO_7 type crystals.[4] No analogue compounds of Ln_3TaO_7 are known in nature. Crystals which were obtained as by-products during the growth are $Pb_3Ta_2O_8$, $Pb_2Ta_2O_7$ and other unidentified crystals.

The growth of the solid solution phases of the $YTaO_4$–

Table 1. List of products obtained by flux method (PbF_2: PbO=80: 20)

Ln[a]	Products (color, shape)
La	$Pb_3Ta_2O_8$(brown, massive), $Pb_2Ta_2O_7$(yellow plates)
Ce	CeO_2(black, octahedral)
Nd	$Pb_3Ta_2O_8$[b]
Sm	$Pb_3Ta_2O_8$[b]
Eu	$Pb_3Ta_2O_8$[b]
Gd	Gd_3TaO_7(yellow plates), $GdTaO_4$(yellow, octahedral)
Dy	$DyTaO_4$(pale yellow, massive)
Y	Y_3TaO_7(pale brown, massive), $Pb_3Ta_2O_8$, $Pb_2Ta_2O_7$
Ho	$Pb_3Ta_2O_8$[b]
Er	Er_3TaO_7(pink plates), $ErTaO_4$(pale yellow, massive)

a) Ln means rare-earth element, the oxide form of which was added as one component of the starting materials. b) Compounds of rare-earth element and tantalum were not obtained.

Table 2. Lattice parameters of products having $LnTaO_4$ and Ln_3TaO_7 composition (1 Å=0.1 nm)

Product	Lattice parameter			
	a(Å)	b(Å)	c(Å)	β(°)
$GdTaO_4$	5.401(2)[a)]	11.060(2)	5.071(2)	95.6(2)
$DyTaO_4$	5.352(2)	10.981(2)	5.060(2)	95.7(2)
$ErTaO_4$	5.313(2)	10.891(2)	5.040(2)	95.7(2)
Gd_3TaO_7	5.321(2)			
Y_3TaO_7	5.240(2)			
Er_3TaO_7	5.321(2)			

a) Numbers in parentheses here are estimated standard deviations in units of the last significant digit.

$YNbO_4$ series has been attempted in the temperature region below 1500 °C. Single phase crystals have been obtained for the compositions $YTa_xNb_{1-x}O_4$ with $x<0.5$. Here, the value x means the composition of the starting materials. For $x\gtrsim0.5$, products showing X-ray patterns corresponding to fergusonite type structure were not obtained. Significant changes in cell dimensions for the grown solid solutions were not observed within experimental error, but for a parallel increase in specific gravity with an increase in Ta content.

The authors wish to express their thanks to Professor Kozo Nagashima of the University of Tsukuba for his kind support of this work.

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