BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 51 (10), 3077—3078 (1978)

Flux Growth of Double Oxides of Niobium and Rare-earth Elements (Ln_3NbO_7)

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(Received April 24, 1978)

Synopsis. Crystals of double oxides of rare-earth and niobium Ln_3NbO_7, where Ln=Ho, Y, Er, Dy, and La, and those of rare-earth and tantalum Ln_3TaO_7, where Ln=Y, Er, and Gd, were grown by Bi_2O_3–B_2O_3 and PbF_2–PbO fluxes for the Ln_3NbO_7, and by PbF_2–PbO flux for the Ln_3TaO_7. The composition of Ln_3NbO_7 or Ln_3TaO_7 is not yet known in natural minerals.

Double oxides of niobium (or tantalum) and a rare-earth element occur in nature as fergusonite Y(Nb,Ta)O_4 and samarskite $Y_4[(Nb,Ta)_2O_7]_3$ *etc.*[1] These compounds have high melting points of over 2000 °C, which depend mainly upon the component ratios between Nb and Ta in the solid solution. We reported that a series of compounds $LnNbO_4$[2,3] and $LnTaO_4$ were able to be grown by the flux method at lower temperatures than 1300 °C. These oxide compounds are attractive materials due to their electro-optical and/or ferroelastic characters,[4] in addition to the possibility of being a new laser matrix. We are now attempting the flux growth of compounds which have a different atomic ratio between the rare-earth element and niobium (or tantalum) than the naturally known minerals. This report describes the syntheses of Ln_3NbO_7 and Ln_3TaO_7 type compounds.

Mixtures of Ln_2O_3 (purity 4N) and Nb_2O_5 (purity 4N) with the molar ratio of 3: 1 were used as starting materials. Fluxes were added to the starting materials in the molar ratio of several to tens of times. The flux systems where we tried to grow Ln_3NbO_7 and Ln_3TaO_7 type crystals were PbF_2–PbO, Bi_2O_3–B_2O_3, B_2O_3–$Na_2B_4O_7$, Bi_2O_3–V_2O_5, and Li_2O–MoO_3. The purity of PbF_2 and PbO was 99.9%, and the others were all of the analytical reagent grade.

The starting material was put in a platinum crucible together with one of the flux materials, and was covered tightly by a platinum lid. This was placed in an electric muffle furnace at 1300 °C and was kept for 2 to 5 h at the same temperature. After that it was cooled slowly down to 900 °C in the rate of 1 to 5 °C/h by a programmed controller. At the final temperature it was taken out of the furnace and was air quenched to room temperature. Products in the crucible were washed with hot diluted HNO_3 for several hours. Crystals thus obtained were identified with the desired materials by X-ray powder diffraction.

The crystals of Y_3NbO_7 are shown as an example in Fig. 1. They are mostly octahedrons in shape and come to about 2 mm in the largest distance. Products obtained by the use of different fluxes are listed in Table 1. Crystals having Ln_3NbO_7 composition were obtained both from the flux systems of Bi_2O_3–B_2O_3 (the flux ratio ranges from 10: 0 to 8: 2) and from PbF_2–PbO (9: 1 to 7: 3). A list of Ln_3NbO_7 and Ln_3TaO_7 type compounds obtained in this work is given in Table 2. Compounds Ln_3TaO_7 were grown using the PbF_2–PbO flux system (from 9: 1 to 7: 3). The growth of crystals containing other rare-earth elements than those listed in Table 2 has not yet been successful. In the course of the runs, $Pb_2Nb_2O_7$ (pyrochlore type structure), $Pb_3Nb_2O_8$, and $LnNbO_4$ type crystals were obtained as by-products.

Precession and Weissenberg photographs show that the crystals given in Table 2, except for La_3NbO_7,

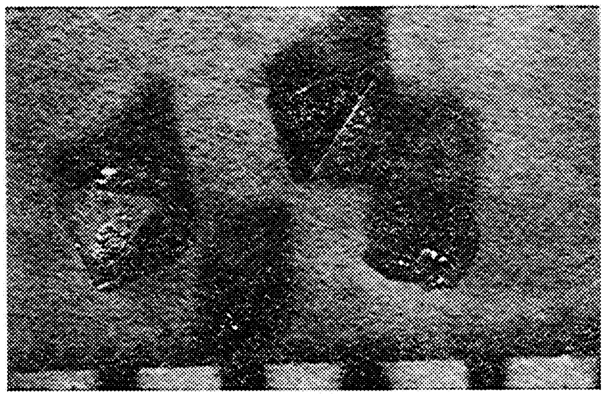

Fig. 1. Crystals of Y_3NbO_7. (1 division=1 mm.)

TABLE 1. FLUX SYSTEMS USED AND THEIR PRODUCTS (STARTING MATERIALS ARE Y_2O_3 AND Nb_2O_5 IN 3: 1 MOLAR RATIO)

Flux	Products
PbF_2–PbO	Y_3NbO_7, $YNbO_4$
Bi_2O_3–B_2O_3	Y_3NbO_7
B_2O_3–$Na_2B_4O_7$	$NaNbO_3$
Bi_2O_3–V_2O_5	$V_3Nb_{17}O_{50}$
Li_2O–MoO_3	$LiNbO_3$

TABLE 2. LIST OF PRODUCTS HAVING Ln_3NbO_7 AND Ln_3TaO_7 COMPOSITION

Compound	Color	Crystal system	Lattice parameter		
			a (Å)	*b* (Å)	*c* (Å)
Ho_3NbO_7	brown	cubic	5.243(3)		
Y_3NbO_7	yellow	cubic	5.238(3)		
Er_3NbO_7	pale brown	cubic	5.252(2)		
Dy_3NbO_7	brown	cubic	5.259(2)		
La_3NbO_7	brown	ortho-rhombic	7.615(2)	7.761(2)	11.14(2)
Y_3TaO_7	pale brown	cubic	5.240(2)		
Er_3TaO_7	pink	cubic	5.251(2)		
Gd_3TaO_7	yellow	cubic	5.321(2)		

belong to a cubic system with the space group of Fm3m. La_3NbO_7, however, belongs to the orthorhombic system with the space group of Pnma. Crystal structure analysis both for the products and for by-products are now in progress.

The authors are grateful to Professor Kozo Nagashima for his kind support of this work.

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