A New Modification of $TiTe_3O_8$

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A metastable modification of $TiTe_3O_8$ is formed, for some heating rates, from an amorphous material prepared by the simultaneous hydrolysis of titanium isopropoxide and tellurium tetrachloride. It has a hexagonal unit cell with $a = 10.764 \pm 0.002$ Å and $c = 5.142 \pm 0.002$ Å. The hexagonal-to-cubic phase transformation occurs at 525—570 °C.

Titanium tritellurate(IV), $TiTe_3O_8$ (cubic), is the only compound in the system TiO_2–TeO_2. It is difficult to form pure $TiTe_3O_8$ by the solid-state reaction of TiO_2 and TeO_2 because volatilization of TeO_2 occurs rapidly at high temperatures. Few investigations[1,2] have been reported on the formation of $TiTe_3O_8$. Bayer[1] heated mixtures of TiO_2 and TeO_2 for 20 h between 600 and 700 °C in the TeO_2-rich region and obtained $TiTe_3O_8$ which was indexed on a cubic unit cell with $a = 10.90 \pm 0.01$ Å. Galy and Meunier[2] indicated that $TiTe_3O_8$ possessing a deformed calcium fluoride structure was formed by heating a stoicheiometric mixture of TiO_2 and TeO_2 for 12 h at 700 °C. Later they[3] analyzed closely the structure of a single crystal grown by a fusion technique; the lattice parameter was estimated as $a = 10.956 \pm 0.003$ Å. Thus, heating for a long period of time at 600—700 °C was required for the formation of $TiTe_3O_8$.

In the present study, it was found that a metastable modification of $TiTe_3O_8$ is formed, for some heating rates, from an amorphous material prepared by the simultaneous hydrolysis of titanium isopropoxide and tellurium tetrachloride. The present paper deals with the formation and transformation of $TiTe_3O_8$.

Experimental

Materials and Procedures.—Titanium isopropoxide $Ti(OC_3H_7)_4$ (99.9% pure) and tellurium tetrachloride $TeCl_4$ (>99% pure) were used as received (Nakarai Chemicals Ltd., Kyoto); they were dissolved in propan-2-ol. A solution of these (in the mole ratio $Ti^{4+}:3Te^{4+}$) was refluxed for 3 h and then hydrolyzed by adding conductivity water at room temperature. The temperature was slowly increased to 75 °C while the resulting suspension was stirred. The hydrolysis product was separated by filtration, washed 20 times in hot water, and dried at 120 °C under reduced pressure. The powder obtained was termed the 'starting powder'.

Measurements.—The starting powder for electron microscopic observation was dispersed in amyl acetate (pentyl acetate) by ultrasonic treatment for 5 min. The dispersed drops were dried on a carbon film, and observed under a 35 keV (*ca.* 5.6×10^{-15} J) beam. Thermogravimetric and differential thermal analyses (t.g.a. and d.t.a.) were carried out in air at a variety of heating rates; α-alumina was used as reference for the d.t.a. The starting powder and specimens obtained from the d.t.a. studies were examined by means of high-temperature *X*-ray diffractometry using nickel-filtered Cu-K_α radiation. Infrared spectroscopy was performed on a dispersion in potassium bromide using the pressed-disc technique.

Results and Discussion

Characterization of Starting Powder.—The starting powder was amorphous, and its average particle size was *ca.* 0.3 µm. The i.r. spectrum of the starting powder showed two absorption bands at 770 and 665 cm^{-1}; it was very similar in shape to the spectrum of the $BaTeO_3$ glass, rather than the $TiTe_3O_8$ glass.[4] According to the data of Dimitriev *et al.*,[4] the $BaTeO_3$ glass,

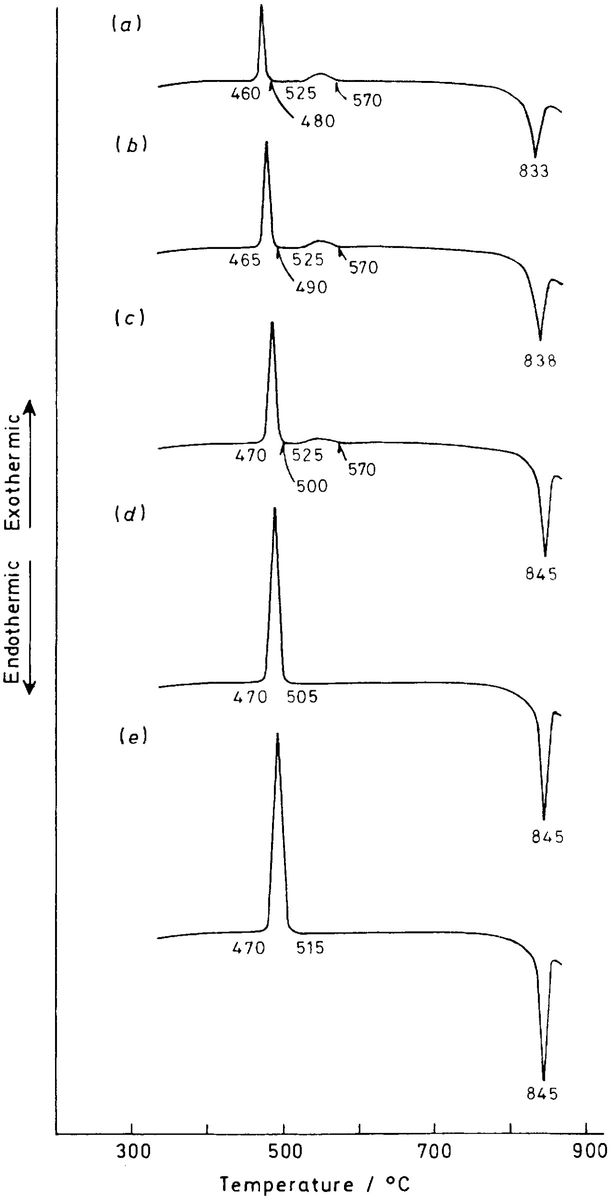

Figure 1. Differential thermal analysis curves for the starting powder at various heating rates: (*a*) 2, (*b*) 5, (*c*) 10, (*d*) 15, and (*e*) 20 °C min^{-1}. Sample weight = 35 mg

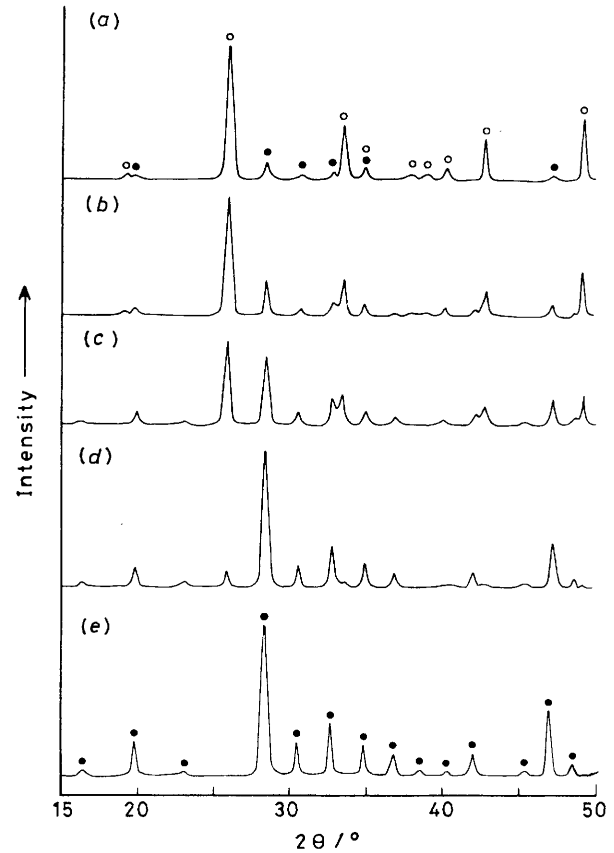

Figure 2. High-temperature *X*-ray diffraction patterns for specimens after crystallization at various heating rates: (*a*) 480, 2; (*b*) 490, 5; (*c*) 500, 10; (*d*) 505, 15; and (*e*) 515 °C, 20 °C min^{-1}. (○) New modification, (●) cubic modification

Table. *X*-Ray data for the new modification of $TiTe_3O_8$*

$d_{obs.}$/Å	$d_{calc.}$/Å	I/I_0	*hkl*
4.66	4.66	5	200
3.456	3.453	100	201
2.692	2.691	40	220
2.584	2.585	10	310
2.385	2.384	5	221
2.330	2.330	5	400
2.251	2.251	10	202
2.123	2.123	25	401
1.859	1.859	45	222

* Hexagonal; $a = 10.764 \pm 0.002$, $c = 5.142 \pm 0.002$ Å.

built up of TeO_3 groups, is characterized by an intense band in the range 680—665 cm^{-1}. On the other hand, the $TiTe_3O_8$ glass, containing TeO_4 groups, is characterized by the presence of an intense maximum at 670—665 cm^{-1} and a shoulder at 625—620 cm^{-1}. No shoulder at 625—620 cm^{-1} was present in the starting powder. Accordingly, the structure of the starting powder can be built up of TeO_3 groups.

Thermal Analysis.—Thermogravimetric examination of the starting powder at a heating rate of 20 °C min^{-1} showed a weight loss of 6.2% up to 265 °C. This can be attributed to the loss of surface-adsorbed propan-2-ol, adsorbed water, and hydrated water.[3]

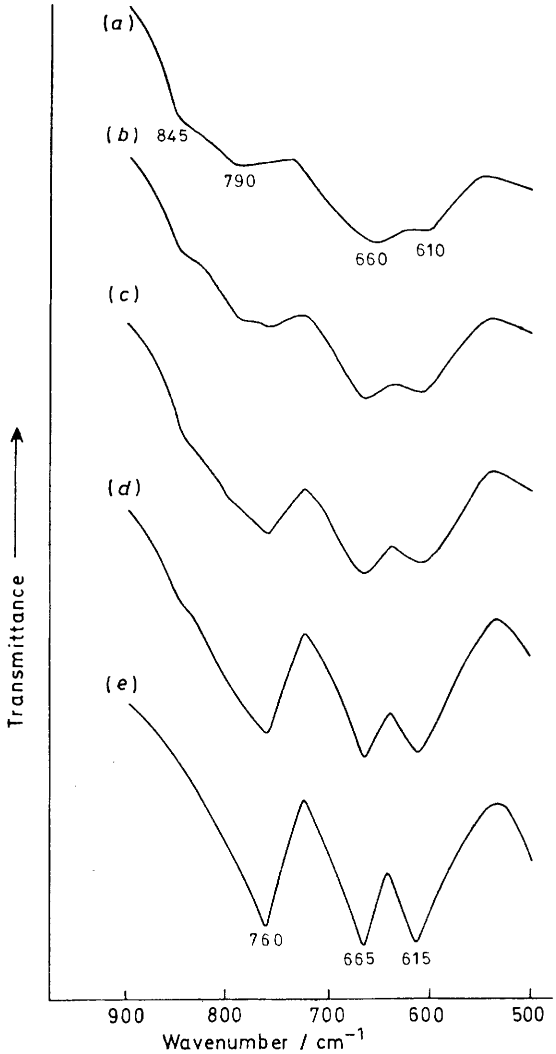

Figure 3. Infrared spectra for specimens obtained by quenching after crystallization at various heating rates, (*a*)—(*e*) correspond to heating conditions as shown in Figure 2

Figure 1 shows the d.t.a. curves for the starting powder at a variety of heating rates [(*a*), 2; (*b*), 5; (*c*), 10; (*d*), 15; and (*e*), 20 °C min^{-1}]. The thermal behaviour was classified into two groups: (*i*) (*a*), (*b*), and (*c*), and (*ii*) (*d*) and (*e*). Each group was exemplified by heating the starting powder at the rates for (*a*) and (*e*). When the heating rate was 2 °C min^{-1}, the d.t.a. curve revealed two exothermic and one endothermic peaks [Figure 1(*a*)]. The first exothermic peak at 460—480 °C, as described later, was found to result from the simultaneous crystallization of the new modification of $TiTe_3O_8$ and the cubic one. The second exothermic peak at 525—570 °C was due to transformation of the new modification to the cubic phase. The endothermic peak at 833 °C results from melting of $TiTe_3O_8$.

At 20 °C min^{-1} [Figure 1 (*e*)], the sharp exothermic peak was observed at 470—515 °C; this was confirmed to result from crystallization of only the cubic modification. The cubic modification melted at 845 °C; this temperature is in agreement with that reported previously.[2]

As can be seen from Figure 1, with increasing heating rate the sharp exothermic peaks resulting from crystallization were shifted to higher temperatures, and the peak height and width increased. Small exothermic peaks due to transformation were observed at heating rates of 2, 5, and 10 °C min^{-1}; however, the peak height reduced with increasing rate. No peak was detected during cooling from 515 and 700 °C, prior to melting.

X-Ray Analysis.—The starting powder, being amorphous, showed no significant change in structure up to the temperatures of the sharp exothermic peaks, regardless of the heating rate. After the sharp exothermic peak at the rate of 2 °C min^{-1}, the specimen at 480 °C gave an *X*-ray diffraction pattern resulting from a mixture of the hitherto undescribed modification of $TiTe_3O_8$ and the cubic one [Figure 2(*a*)]. After the small exothermic peak, the specimen at 600 °C showed the characteristic pattern of the cubic modification.[6] No other species were observed throughout the heating process. During cooling, the cubic form did not transform to the new modification. Clearly, the new modification must be metastable.

The *X*-ray data for the new modification obtained by quenching after heating for 30 min at 480 °C are presented in the Table. The goniometer scanning speed of 0.25° min^{-1} was selected so as to achieve *d* spacings. All diffraction lines were indexed as a hexagonal unit cell with $a = 10.764 \pm 0.002$ Å and $c = 5.142 \pm 0.002$ Å. High-temperature *X*-ray diffraction patterns of the specimens after crystallization, at other heating rates, are shown in Figure 2 (*b*)—(*e*). The intensity of the lines of the cubic modification increased with increasing heating rate, in inverse proportion to that of the hexagonal lines. The lines of the hexagonal modification, when heated at 15 °C min^{-1}, were barely observed, as shown in Figure 2(*d*), although in the d.t.a. curve no peak due to transformation was detected. The pure cubic modification crystallized at 20 °C min^{-1}. From the abovementioned results, it is obvious that formation of the hexagonal modification depends strongly on the heating rate. It could not, however, be obtained as a single phase although experiments at a heating rate of 1 °C min^{-1}, and isothermal treatments, were performed.

Infrared Spectra.—Figure 3 shows the i.r. spectral patterns for the specimens obtained by quenching after crystallization at each heating rate. It is difficult to determine spectroscopically whether tritellurate compounds are built up of TeO_4 or TeO_3 groups, because the locations of the main characteristic bands, between 800 and 600 cm^{-1}, are similar. However, use of the absorption bands at 845 and 790 cm^{-1} is more informative. The spectral pattern of the specimen containing a large amount of the hexagonal modification is very similar to that of $V_2Te_2O_9$,[7] built up of TeO_3 groups [Figure 3(*a*)]. Both bands at 845 and 790 cm^{-1} decreased in intensity with increasing amount of the cubic modification [Figure 3(*b*)—(*d*)]. Finally, they disappeared in the spectrum of the pure cubic modification, consisting of TeO_4 groups [Figure 3(*e*)].[7,8] From these results, the hexagonal modification is built up of TeO_3 groups.

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