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The Nonstoichiometry of Gadolinium Ditelluride

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The following compounds are found in the rare earth-tellurium system:[1-3] LnTe, Ln_3Te_4, Ln_2Te_3, Ln_4Te_7, $LnTe_2$, $LnTe_3$, and $LnTe_4$, where Ln=rare earth elements. In these tellurides, the ditellurides have the tetragonal lattice (Fe_2As type). In the La–Te[2] and Nd–Te[4] systems, the ditellurides are stable over a large homogeneity range. The *a* parameter of the ditellurides, in both systems, increases monotonously with the increase in Te content in the homogeneity range represented by the $LnTe_{2\pm x}$ formula. The *c* parameter of the lanthanum ditelluride decreases in the monotone with the increase in the content, but in the neodymium ditelluride it has a minimum value at the composition of $NdTe_{1.96}$.

In the case of heavier rare earth elements than gadolinium, there have been few investigations of the nonstoichiometric properties of the ditellurides. In this article the preparation of pure gadolinium ditellurides and their nonstoichiometric properties will be described.

Experimental

The gadolinium was prepared in our laboratory by the calcium reduction of GdF_3 in tantalum containers under a purified argon atmosphere, and was then refined by arc-melting and electron-beam melting. The purity of the gadolinium obtained by this method was approximately 99.9%. Tellurium of 99.999% purity was obtained from Wako Chemical Industies, Ltd., Tokyo. The gadolinium ditellurides were prepared in double-compartment quartz tubes.

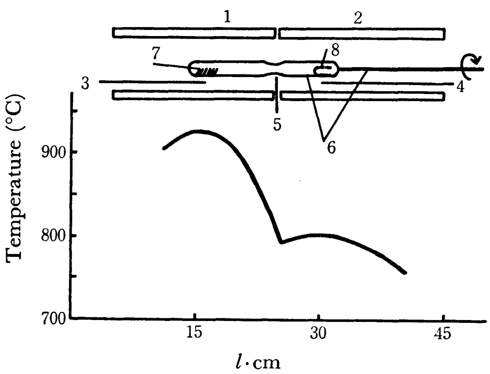

Fig. 1. Temperature distribution in the separate two-zone furnace. 1, 2) furnace; 3, 4, 5) thermocuples; 6) quarz tube and bar; 7) tellurium; 8) Ta boat and gadolinium metal

Finely-ground gadolinium was placed in one side and tellurium in the other side. Gadolinium was placed in tantalum crucibles in order to avoid direct contact with the quartz tube. In this way, the direct contact of gadolinium and tellurium, which might cause an explosion, was avoided. After the evacuating of the quartz tube to 10^{-5} mmHg, the tube was sealed and placed in a horizontal tublar furnace which had two heating zones. A sketch of the reaction apparatus and the temperature distribution in the separated two-zone furnace are shown in Fig. 1. The sealed quartz tube in the furnace was rotated at the rate of 50—100 rpm/min. The temperature of the gadolinium part was raised to 800°C from room temperature at a heating rate of 200°C/hr. The temperature of the tellurium part was 100—150°C higher than that of the gadolinium side. The quartz tube was held under the given conditions for 7—10 hr, until the tellurium had completely reacted, and was then cooled slowly to room temperature. The samples were investigated by chemical and X-ray analysis. The prepared powder was homogenous in its external appearance. The X-ray powder patterns were taken with a Debye-Scherrer camera using FeK_α radiation. These patterns were used to identify the phase present in polyphase samples and to determine the lattice parameters. The densities of the samples were determined by means of a pycnometer.

Results and Discussion

The powder of $GdTe_2$ shows a dark-violet color. From the X-ray diffraction pattern of $GdTe_2$, this phase appeared to be isostructural with the previously-reported tetragonal $GdTe_2$[3] (Fe_2As type). The lattice parameters of the stoichiometric $GdTe_2$ were a= 4.317 Å, c=8.951 Å, and c/a=2.073.

In order to determine the range of the homogeneity of $GdTe_{2\pm x}$, samples were synthesized in the composition range of $GdTe_{1.7}$–$GdTe_{2.2}$ (63 at% to 68.7 at% of Te). For the gadolinium-rich side, the limit of the homogeneity phase was situated at approximately $GdTe_{1.77}$ (63.8 at% Te). A sample containing 63.6% Te ($GdTe_{1.75}$) was composed of two phases, a rhombic lattice (Gd_2Te_3) and a tetragonal lattice ($GdTe_2$). A sample containing 64.0 at% Te ($GdTe_{1.78}$) was constituted of pure $GdTe_{2-x}$ with a tetragonal lattice. On the tellurium-rich side, the limit of homogeneity was located at the composition of $GdTe_{2.10}$ (67.7 at% Te). In more tellurium-rich side, both phases, $GdTe_{2+x}$ and $GdTe_3$, appeared. These experimental results make it clear that the homogeneity range of $GdTe_{2\pm x}$ is situated from $GdTe_{1.77}$ to $GdTe_{2.10}$. The lattice parameter varied conspicuously with the variation in the nonstoichiometric composition, but the relation between them was not linear. The variations in the lattice parameters and c/a ratio are plotted against the Te/Gd atomic ratio in Fig. 2. The figure shows that the lattice parameter, *a*, increases with an increase in the

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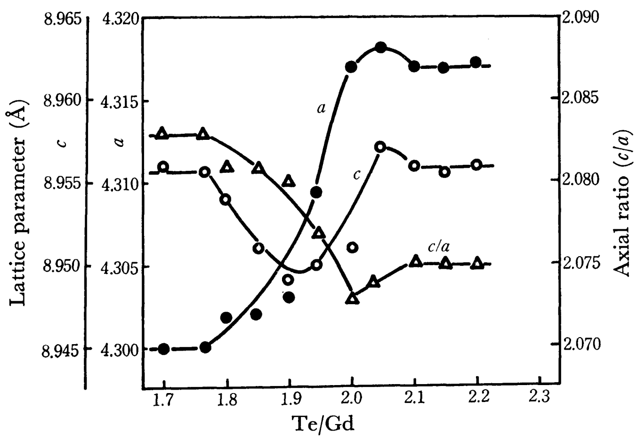

Fig. 2. The variation of the lattice parameters and the axial ratio against Te/Gd ratio in gadolinium detelluride.

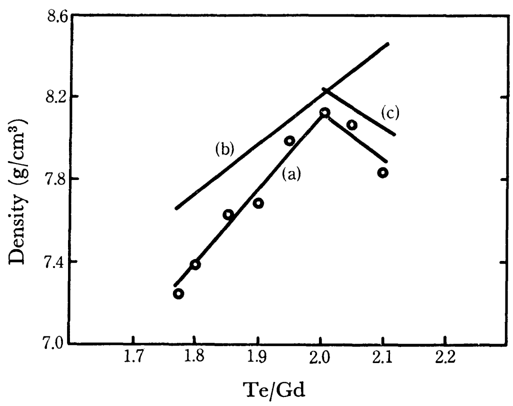

Fig. 3. The variation of density against nonstoichiometric composition of gadolinium ditelluride. (a): experimental value, (b) and (c): X-ray density calculated on the assumption of $GdTe_{2\pm x}$ or $Gd_{1-x}Te_2$, respectively.

tellurium concentration and that the lattice parameter, *c*, reaches its minimum value at the composition of $GdTe_{1.92}$. The relation between the axial ratio, *c*/*a*, and concentration ratio, Te/Gd, shows an anomaly at the composition of $GdTe_{2.0}$. From these facts, it may be seen that the types of defects in the crystal structures are different between the two regions of Te/Gd$<$2 and Te/Gd$>$2.

In Fig. 3 the variation in the densities in the homogeneity range is plotted against the Te/Gd ratio. The line (a) shows the experimental values. The lines (b) and (c) are the densities calculated on the assumption that the nonstoichiometric composition can be indicated by the $GdTe_{2\pm x}$ formula and the $Gd_{1-x}Te_2$ formula respectively. The experimental results show the same tendency as the values of the line (b) in the region of Te/Gd$<$2 and the same as the values of the line (c) in the region of Te/Gd$>$2.

From these variations in the lattice parameters, the axial ratio, *c*/*a*, and the densities, it seems probable that tellurium vacancies form in the region of Te/Gd$<$2 and that gadolinium vacancies from in the region of Te/Gd$>$2. Therefore, the homogeneity range of the gadolinium ditelluride is located form $GdTe_{1.77}$ to $Gd_{0.95}Te_2$.

Lin and Steinfink[4] investigated the neodymium ditelluride. According to their work, the variation in the lattice parameters of neodymium ditelluride appeared in the homogeneity range of $NdTe_{1.75}$ to $NdTe_{2.10}$. The tendency of the variation in the lattice parameters is similar to that of gadolinium ditelluride, which was studied in our experiment. It may be seen that the homogeneity range of the neodymium ditelluride is located from $NdTe_{1.75}$ to $Nd_{0.95}Te_2$.