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## D11

## A Study of Decomposition of $Ce(In_{1-x}Sn_x)_3$ in Air Accompanied by Whisker Growth and Measurement of Electrical Resistivity

J. SAKURAI*, S. TAKEDA and Y. KOMURA

*Faculty of Science, Hiroshima University, Higashi-senda-machi, Naka-ku, Hiroshima, 730, Japan*

$CeSn_3$ is an interesting compound which shows the mixed valence phenomena. One of the complexities in this sample is that it decomposes rapidly in air. For example, a contradiction in Mössbauer measurements by different groups on this sample was considered to originate from this decomposition [1]. Thus we must be careful in understanding its properties.

The purpose of the present study is to see how the decomposition of $CeSn_3$ and its pseudo-binary alloys, $Ce(In_{1-x}Sn_x)_3$, actually progresses, and to see how the decomposition is reflected on the electrical resistivity.

Ingots of samples are prepared by arc-melting in Ar atmosphere. X-ray powder diffraction showed that all samples of $Ce(In_{1-x}Sn_x)_3$ except pure $CeSn_3$ are of a single phase having a cubic $Cu_3Au$ type crystal structure.

In the sample of $CeSn_3$, diffraction peaks due to $\beta$-Sn as an impurity phase were observed in addition. Content of $\beta$-Sn was found to change drastically with the time elapsed from the powder preparation. X-ray counts, at $\beta$-Sn diffraction position, of a quickly prepared powder are at the background level for the first several minutes and then gradually increase. Peak intensities of $\beta$-Sn are already comparable to those of $CeSn_3$ after a couple of hours. Peaks of $CeSn_3$ completely disappear and only those of $\beta$-Sn replace them after two days. The decomposition of $CeSn_3$ in air and the accompanying precipitation of $\beta$-Sn progress rapidly. Ce atoms are supposed to be oxidized and/or hydrated to form an amorphous material unobservable by X-ray diffraction. Decompositions of all samples $Ce(In_{1-x}Sn_x)_3$ except $CeSn_3$ are found to be much slower.

Ingots of $CeSn_3$ kept in a glass tube under a vacuum of $10^{-6}$ torr stay shiny for months. On the other hand, ingots of $CeSn_3$ in air lose rapidly the metallic lustre and in a few days they look like covered with fur or mould. Under an optical microscope, the ingots are seen to be covered with a flock of small fragments with irregular shapes mixed with strictly straight rods.

These rods were picked up and observed under a transmission electron microscope. They turned out to be $\beta$-Sn whiskers; electron diffraction patterns have tetragonal symmetry and lattice constants, *a* and *c*, agree with the reported values of $\beta$-Sn with the rod axis along [101] crystallographic direction. Size of these whiskers varies; the diameter is typically of 0.5–1.0 μm and the length is 1 mm at most. Thus, a part of $\beta$-Sn decomposed from $CeSn_3$ is found to exotically grow into whisker.

Ingots of $Ce(In_{1-x}Sn_x)_3$ whith $x \neq 0$ keep shiny for longer period. Rare whiskers are found on ingots of $CeIn_3$. Still rarer whiskers are found on ingots of $Ce(In_{1-x}Sn_x)_3$ with x neither 1 nor 0

We have also observed the ingot surface by a scanning electron microscope. Whiskers with length of several hundred μm are observed on a fresh surface of $CeSn_3$ cracked only several minutes before. This fact shows the rate of growth of the whiskers is very rapid. Besides, numerous eruptions with diameter of about 1 μm are observed on the fresh surface of $CeSn_3$ as well as all other samples of $Ce(In_{1-x}Sn_x)_3$. They look like pebbles under the scanning electron microscope. Probably some eruptions somehow gain their heights and are thought to develop into whiskers.

We have measured electrical resistivity $\rho$ of $Ce(In_{1-x}Sn_x)_3$. Samples of a typical dimension 1 X 1 X 15 $mm^3$ are cut from the ingots. Measurements were made by the standard dc four prove method. As the decrease of temperature, $\rho$ of all samples $Ce(In_{1-x}Sn_x)_3$ was found to decrease sharply at a critical temperature around 4.2 K. Fig. 1 shows several examples. $Ce(In_{0.4}Sn_{0.6})_3$ looks like as if it were

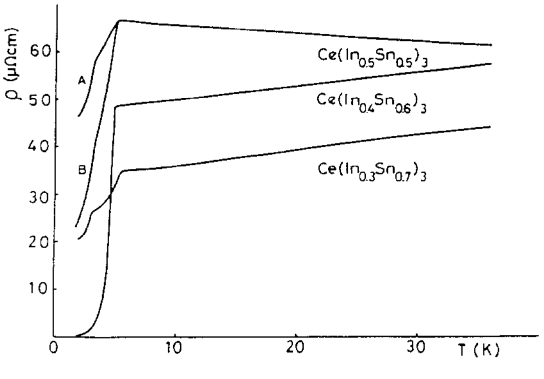

Fig. 1. Electrical resistivity $\rho$ of three samples of $Ce(In_{1-x}Sn_x)_3$ plotted as a function of temperature T.

superconductor; $\rho$ suddenly decreases below 5.5 K and tends to zero below 2 K. Nevertheless, the amount of the decrease of $\rho$ is found to depend on the surface state. The sample which is gently rubbed by a soft tissue paper so that it becomes more shiny immediately before mounting on the sample holder, has much smaller decrease of $\rho$. This is shown for $\rho$ of $Ce(In_{0.5}Sn_{0.5})_3$. Curve A is with this rubbing and curve B is without. Thus we conclude that the superconducting state is not due to bulk sample, but is due to deposits of In–Sn alloy on the sample surface. These deposits are likely to be the eruptions on the sample surface observed by scanning electron microscope. In $Ce(In_{0.3}Sn_{0.7})_3$, the decrease of $\rho$ is clearly seen to have two steps. This is understood because the In–Sn alloy is eutectic and $In_{0.3}Sn_{0.7}$ consists of two components with different compositions and with different superconducting temperatures. The values of these two temperatures are near to those reported [2] on In–Sn alloys, and prove a small amount of this alloys actually deposited on sample surface.

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## D12

# A New Family of Sheet Structures: the Oxyselenides Formed by a Rare Earth and a Second Metal

S. BÉNAZETH, J. FLAHAUT*, M. GUITTARD and P. LARUELLE

*Laboratoire de Chimie Minérale Structurale associé au CNRS, Faculté de Pharmacie, 4, avenue de l'Observatoire, F75270 Paris Cédex 06, France*

Sheet structures are observed in oxyselenides formed by La and a second metal of the IIIA–VA groups of the periodical classification.

$$\left.\begin{array}{l}(LaO)GaSe_2\\(LaO)InSe_2\end{array}\right\}$$ orthorhombic pseudo tetragonal cells of the $(LaO)GaSe_2$ type

$(LaO)_4Ge_{1.5}Se_5$: orthorhombic cell of the $(NdO)_4$-$Ga_2S_5$ type, with disordered arrangement of Ge atoms on the Ga sites.

$(LaO)_2SnSe_3$: orthorhombic pseudo tetragonal cell of the $(LaO)_2SnS_3$ type.

$(LaO)SbSe_2$: tetragonal cell of the $(CeO)BiS_2$ type.

All these structures are formed by alternating (LaO) sheets and $(M_xSe_y)$ sheets (M = second metal). The (LaO) sheets are formed by $La_4O$ tetrahedra which share 4 of their 6 edges in a tetragonal or pseudo tetragonal arrangement. The $(M_xSe_y)$ sheets are formed by 2, 3 or 4 layers of Se atoms. The M atoms are only bonded to Se atoms, in octahedral (Sb) or tetrahedral (Ga, In, Ge, Sn) arrangements. Similar compounds are not obtained with the other rare earths. The structure of $(LaO)GaSe_2$, which is only observed with selenides, is described: the cell is orthorhombic space group $P2_1ab$; $a = 5.951(3)$; $b = 5.963(3)$; $c = 12.256(7)$ Å; $Z = 4$; $d_x = 5.84$ Mg m$^{-3}$; $M$ (MoK$\alpha$) = 31.3 mm$^{-1}$.

The structure was established on single crystal data and refined by a least-squares procedure; the final R value is 0.07 on 523 independent reflections. The structure is formed by alternating (LaO) and $(GaSe_2)$ layers, parallel to the (001) plane.

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## D13

# Lanthanide Oxides: Effect of $CO_2$ on the $Yb_2O_3$ Hydration

I. CARRIZOSA, J. A. ODRIOZOLA, J. M. TRILLO

*Inorganic Chemistry Department, Faculty of Pharmacy, University of Seville, Seville, Spain*

and M. F. EBEL

*Institut fur Angewandte und Technische Physik. Technische Universität Wien, Vienna, Austria*

Recent results in our laboratory [1, 2] have proved that the heaviest terms of the 4f series oxides undergo bulk hydration and carbonation when exposed to the atmospheric air, in contradiction with the previous literature [3]. The main difference between the lighter and the heavier 4f oxides is related to kinetic aspects.

In the case of the hydration of the $La_2O_3$, Rosynek [4] has shown a certain inhibition effect exerted by the $CO_2$. In the present paper, the interaction of the $Yb_2O_3$ with $H_2O$, $H_2O/CO_2$ mixtures and atmospheric air has been examined through XPS and TPD measurements. The effect of $CO_2$ on the hydration of ytterbium sesquioxide is discussed in the light of those results.

Ytterbium hydroxycarbonate was precipitated with $NH_3$ from nitrate solutions. $Yb_2O_3$ was finally prepared by calcining the precipitate in air at 873 K. The sample here studied was characterized by X-ray diffraction, thermogravimetric (TG) and differential thermal analyses (DTA), IR spectroscopy and pore size distribution. Data about preparation and characterization are reported in [1].

Details concerning the temperature programmed decomposition (TPD) device are given in [5]. All the experiments were carried out in helium flow (30 ml