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SECTIONS OF TERNARY DIAGRAMS RARE EARTHS–INDIUM–TIN OF $R(In_{1-x}Sn_x)_3$ COMPOSITION

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Results of thermal studies on $Nd(In_{1-x}Sn_x)_3$ and $Gd(In_{1-x}Sn_x)_3$ solid solutions are reported, together with those of structural studies on $R(In_{1-x}Sn_x)_3$ (R = Nd, Sm, Gd, Tb, Dy, Er, Tm). The non linear behaviour of the lattice parameters and the shape of the phase diagrams are compared. The peritectic decomposition of tin-rich phases of $Gd(In_{1-x}Sn_x)_3$ is pointed out. The necessity of high pressure studies of these solid solutions is outlined.

The compounds of formula RM_3 (R = rare earths; M = In, Sn) crystallize in the cubic $AuCu_3$ type structure [1], but RSn_3 phases can be synthesized at standard pressure only to gadolinium, with the exception of $YbSn_3$ [2]. Miller & Hall [3], however, were able to synthesize under increasingly higher pressures also $TbSn_3$, $DySn_3$, $HoSn_3$ and $ErSn_3$. At room temperature and pressure these phases are isotypic with the other rare earth tritin compounds and a strong correlation between the cell parameters of the RSn_3 compounds and the ionic (3+) radii of the rare earth elements can be found [3, 4].

The purpose of this work is to investigate the variation of the lattice parameter in $R(In_{1-x}Sn_x)_3$ solid solution *vs.* the tin content, and to correlate such a variation with the shape of the corresponding phase diagram.

Experimental

The starting materials used to prepare the alloys were In and Sn (5N pure) and R (2N5 pure), obtained from Koch–Light Co.

The samples (each of a mass of about 1 g) were obtained by direct synthesis. The two metals were compressed together and sealed in Mo crucibles under pure argon and were melted in an induction furnace while being carefully shaken to ensure homogeneity. This method avoided the necessity of chemical analysis of the samples as no losses were sustained. Differential thermal analysis (DTA) was performed for each alloy at heating and cooling rates of 5 or 10 deg/min (the accuracy was ± 5 deg).

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In a few cases to ensure thermal equilibrium lower cooling rates were necessary. In other cases annealing treatments were also performed.

The alloys showed a grey metallic lustre; the oxidizability increased regularly with decreasing indium content. The microstructures of as-cast or heat treated alloys were examined using standard metallographic techniques. The microhardness of the alloys was determined by the Vickers' method using a Leitz–Durimet hardness tester. The load used was 25 grams.

The crystal structure analyses were performed by means of the powder method, using Cu K_α radiation. The intensity calculations for the powder patterns were carried out using the Lazy Pulverix program [5].

Results and discussion

As the structure of the pure components of RM_3 is the same, the chemical properties are similar and the lattice parameters are only slightly different ($\sim 1\%$), we can expect complete solubility between RIn_3 and RSn_3, possibly obtained by high pressure synthesis.

An extended solid solubility of the compounds of formula $R(In_{1-x}Sn_x)_3$ was already pointed out in a previous work [6] also for R = Tb, Dy, Ho, Er and Tm.

The behaviour of the reticular parameters with the tin content is not linear (i.e. it does not follow Vegard's law) for all the solid solutions considered (Fig. 1). A well

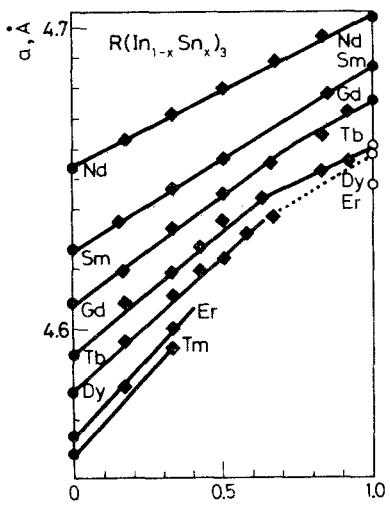

Fig. 1 Trend of the lattice parameters vs. the tin content in the solid solutions $R(In_{1-x}Sn_x)_3$
● = lattice parameters for RM_3 pure components at standard pressure.
○ = lattice parameters for the RSn_3 phases obtained under pressure [3]

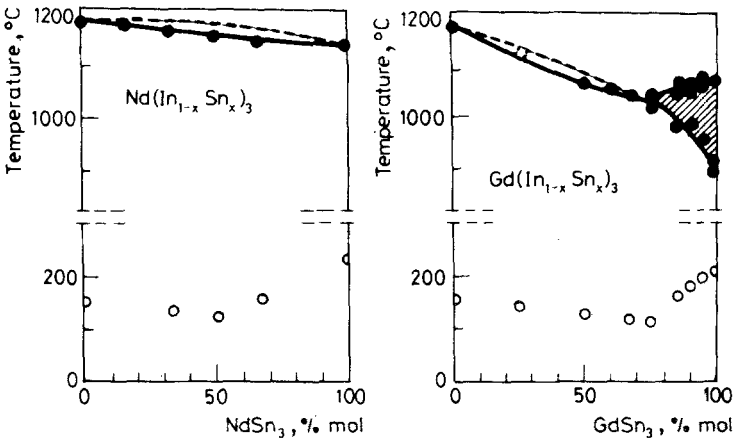

Fig. 2 Isoplethic sections $NdIn_3$—$NdSn_3$ and $GdIn_3$—$GdSn_3$. The dotted area represents the polyphasic region where the phase 1 : 3 is not stable.
○ non-equilibrium thermal effects due to the presence of eutectics RM_3—M

known example of this behaviour is the solid solution $Ce(In_{1-x}Sn_x)_3$ [7], where instead of a single straight line a piecewise-linear behaviour can be found. This trend is probably due to the valence fluctuation of Ce in $CeSn_3$ [8]. A similar behaviour was considered as a proof of the phenomenon of valence fluctuation [9, 10], even if it is only indicative of a second order phase transition [11, 12].

A similar trend can be observed also in other solid solutions of the series $R(In_{1-x}Sn_x)_3$ where valence fluctuation can no longer be invoked (Fig. 1). For this reason we tried to correlate the trend of the cell parameters of the solid solutions $R(In_{1-x}Sn_x)_3$ with the shape of the corresponding section of the phase diagram R–In–Sn.

Figure 2 shows the constitutional phase diagrams of $NdIn_3$–$NdSn_3$ and $GdIn_3$–$GdSn_3$ derived from DTA, X-ray analysis and metallography. Generally the thermal effect of the eutectic RM_3–M can be revealed also on the stoichiometric RM_3 compositions as reported in Figure 2 (faint points at temperatures between 100° and 300°). The disappearance of such a thermal effect, obtained by annealing at intermediate temperatures (i.e. without reaching the melting temperature), assured the homogeneity of the samples, subsequently confirmed by micrographic analysis.

Even if for both $Nd(In_{1-x}Sn_x)_3$ and $Gd(In_{1-x}Sn_x)_3$ complete miscibility exists, the thermal aspect of the two diagrams is quite different: this is due to the fact that $GdSn_3$ forms peritectically. The dotted area on the phase diagram represents the polyphasic region where the phase 1 : 3 does not exist. The study of this region is

beyond the scope of this work. We note that the deviation from the linearity of the reticular parameters of $Gd(In_{1-x}Sn_x)_3$ appears around the same concentration at which there is the passage from the congruent melting to the peritectic formation, but this behaviour must be confirmed for the other cases. In particular it would be useful to obtain solid solutions at high pressures. This will show whether increasing pressure can stabilize an existing peritectic phase of low temperature or allow the synthesis of a new phase.

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Zusammenfassung — Ergebnisse der thermischen Untersuchung der festen Lösungen $Nd(In_{1-x}Sn_x)_3$ und $Gd(In_{1-x}Sn_x)_3$, und der Strukturuntersuchung von $R(In_{1-x}Sn_x)_3$ (R = Nd, Sm, Gd, Tb, Dy, Er, Tm) werden mitgeteilt. Das nichtlineare Verhalten der Gitterparameter und der Verlauf der Phasendiagramme werden verglichen. Die peritektische Zersetzung der zinnreichen Phasen von $Gd(In_{1-x}Sn_x)_3$ wird erörtert. Auf die Notwendigkeit von Hochdruckuntersuchungen dieser drei festen Lösungen wird hingewiesen.

Резюме — Приведены результаты термического исследования твердых растворов $Nd(In_{1-x}Sn_x)_3$ и $Gd(In_{1-x}Sn_x)_3$, наряду с результатами структурных исследований $R(In_{1-x}Sn_x)_3$, где R = Nd, Sm, Gd, Tb, Dy, Er и Tm. Сопоставлено нелинейное поведение параметров решетки и вид фазовых диаграмм. Отмечено перитектическое разложение обогащенных оловом фаз $Gd(In_{1-x}Sn_x)_3$. Указано на необходимость исследования этих твердых растворов при высоких давлениях.