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Structure and thermal stability of the RMgPb rare earth compounds, and the anomalous melting behaviour of SmMgPb

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ABSTRACT

The synthesis, crystal structure and melting behaviour of the new family of ternary rare earth RMgPb compounds is reported in this work. All the rare earth elements (including Y and Sc) form the equiatomic phase 1:1:1 with Mg and Pb, similar to the recently investigated RMgSn compounds series. Unlike RMgSn, all the RMgPb phases (the lighter, as well as the heavier, trivalent lanthanides) crystallize with the same crystal structure: the tetragonal CeScSi-type (an ordered derivative of the La_2Sb-type structure, *tI*12, space group *I*4/*mmm*). Both the observed unit cell volume (V_{obs}) and the mean atomic volume (V_{obs}/n, where n is the number of atoms in a unit cell) decrease linearly from LaMgPb [$a = 4.598(1)$ Å, $c = 16.512(2)$ Å] to LuMgPb [$a = 4.356(1)$ Å, $c = 15.783(2)$ Å] confirming the lanthanide contraction in the RMgPb series. On the other hand, the volume of formation (ΔV %) becomes more negative by a non-linear trend on going from La to Lu. A high temperature polymorph phase, orthorhombic TiNiSi-type, has been found for both YbMgSn and YbMgPb. Further work concerning the existence of the phase "ScMgSn" has been also performed. The relationships between the structural properties and formation thermodynamics of both the RMgSn and the RMgPb series of compounds have been examined in the present work.

All the RMgPb phases form congruently (including YMgPb and ScMgPb) and their melting temperatures decrease non-linearly from LaMgPb to ScMgPb. YbMgSn and YbMgPb also form congruently with anomalously high melting points. A particular and interesting anomaly has been observed for SmMgPb and Sm containing pseudo-ternary compounds [$Nd_{1-x}Sm_xMgPb$ ($x = 0.4, 0.6, 0.8$) and $Sm_{1-y}Gd_yMgPb$ ($y = 0.6, 0.4, 0.2$)]; their melting temperature are lower than the ones expected from the trend established by the other RMgPb phases by as much as 70 °C. This anomalous behaviour led to an examination of the melting points of selected Sm-bearing materials, including Sm metal. The low melting points are thought to be due to a decrease in the valence of trivalent Sm phases at 25 °C as the materials are heated and thus a lower bonding strength.

1. Introduction

Only a limited amount of information is available in the literature on the ternary RMg-X (where X = Ge, Sn, Pb) systems [1–3]. To the best of our knowledge, only the crystal structures of EuMgPb and YbMgPb have been reported for the R-Mg-Pb systems [4]: EuMgPb and YbMgPb crystallize in the orthorhombic TiNiSi and hexagonal ZrNiAl structure type, respectively. The divalent character of Eu and Yb in these two compounds was inferred by comparison with the Ca, Sr and Ba homologous on the basis of crystallochemical considerations [4], even though no magnetic measurements have been performed. In a previous study we have reported on the equiatomic RMgSn intermetallics [5]. These compounds were found to crystallize in two crystal structures: the orthorhombic TiNiSi-type for the lighter R (La, Ce, Pr) and the tetragonal CeScSi-type for all other trivalent lanthanide metals. The observed unit cell volume V_{obs} and the mean atomic volume V_{obs}/n (where n is the number of atoms in a unit cell) both decrease as expected due to the lanthanide contraction, and consequently the volume of formation (ΔV%) becomes more negative on going along the series. On the other hand, the melting temperatures of all the RMgSn compounds, which form congruently, decrease from La to Lu. The relationships between the melting points and the volume of formation with the lanthanide contraction have been examined. The volume of formation trend indicated an increasing thermodynamic stability on going from La to Lu, but this is in contrast with

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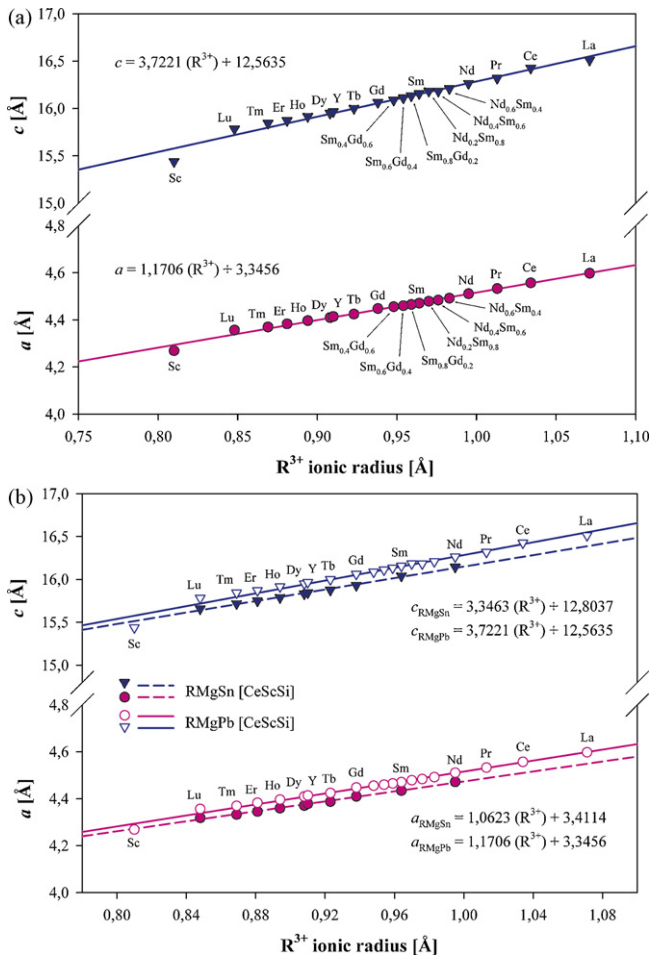

Fig. 1. (a) The lattice parameters *a* and *c* for the trivalent rare earth RMgPb compounds (including the pseudo-ternary alloys) versus the rare earths ionic radius R^{3+}. (b) The lattice parameters for both the RMgSn and the RMgPb families versus the R^{3+} ionic radius. The RMgSn data are from Ref. [5].

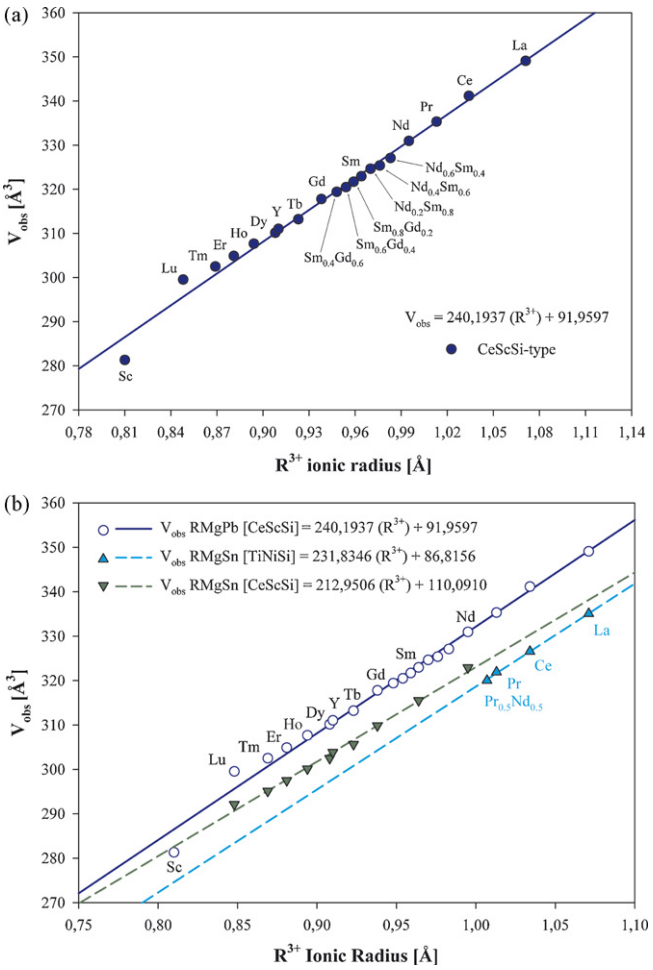

Fig. 2. (a) The observed cell volume (V_{obs}) for the trivalent rare earth RMgPb compounds versus the rare earth ionic radius R^{3+}. (b) The observed unit cell volume of the RMgSn and RMgPb families versus the R^{3+} ionic radius. RMgSn data are from Ref. [5].

the expected behaviour from the lanthanide contraction as determined from the relative volume ratio method [6,7] which predicts that the light lanthanide RMgSn phases are more stable than the heavies. On the contrary, the decreasing trend of the melting temperatures along the series is consistent with the relative volume ratio relationship [6,7].

The present work reports on the crystal structure, melting behaviour and thermal stability of the new RMgPb family of equiatomic compounds and on the relationships among the crystallographic data, volumes of formation and melting points.

2. Experimental procedures

Samples with the nominal equiatomic RMgPb composition were prepared for R = La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Sc and Y. Moreover, the pseudo-ternary alloys $Nd_{1-x}Sm_xMgPb$ ($x = 0.4, 0.6, 0.8$), $Sm_{1-y}Gd_yMgPb$ ($y = 0.2, 0.4, 0.6$), $PrMgSn_{0.75}Pb_{0.25}$, $PrMgSn_{0.5}Pb_{0.5}$, and $SmMgSn_{0.5}Pb_{0.5}$ were also synthesized. The starting metals were purchased from commercial vendors. The rare earth metals were (with respect to the other rare earth metals) 99.9 wt.% pure; the Mg 99.98 wt.% and the Pb and Sn 99.99 wt.% pure. Stoichiometric amounts of the metals (for a total mass of 2–3 g) were placed and pressed into an outgassed tantalum crucible, which was closed by arc-welding under flowing Ar. The samples were melted in high-frequency induction furnace by heating under vacuum up to 1100–1300 °C and shaking to ensure homogenization. A strongly exothermic reaction was observed in all the samples. The crucibles were then sealed under vacuum in quartz tubes and annealed at a temperature between 750 °C and 900 °C for 4–14 days in a resistance furnace. The ScMgPb samples were annealed at 500 °C and 450 °C for 12 and 30 days, respectively. The samples were usually air cooled. No contamination by Ta was observed. The alloys appeared to have been completely melted and had a metallic-gray lustre. They are, however, air sensitive and pyrophoric. All the samples were subjected to X-ray diffraction and differential thermal analysis (DTA), and some of them were examined by a scanning electron microscope (SEM) equipped with microprobe (EDX) for semiquantitative analysis. The pseudo-ternary alloys were prepared as above, they also were generally subjected to DTA analysis either directly in the as-cast form or after some annealing (700–950 °C for 2–19 days). The X-ray investigation was mainly carried out on powders using a Guinier camera with Cu Kα radiation and silicon as an internal standard ($a = 5.4308$ Å); the diffraction patterns were indexed with the aid of LAZY-PULVERIX [8] and the lattice parameters obtained by means of least-square methods. The DTA analysis, to determine the melting behaviour, was performed on 0.5–0.8 g samples of the alloy. The DTA samples were enclosed in Mo crucibles under an Ar atmosphere and then transferred to the DTA equipment. Thermal cycles were carried out at heating rates of 20 °C/min and at 5 °C/min or 10 °C/min on cooling; the temperature was measured with an accuracy of 5 °C.

3. Results and discussion

3.1.1. Crystallographic analysis

All the RMgPb samples were homogeneous and single or nearly single phase; only in few of them (Tm, Lu and Sc samples) a small percent of Mg_2Pb was observed in the X-ray patterns. The Guinier powder patterns of all of the trivalent rare earth RMgPb alloys were fully indexed on the basis of the tetragonal CeScSi-type structure (a ternary, ordered derivative of the La_2Sb-type structure, *tI*12, space group *I*4/*mmm*, $Z = 4$) and accurate unit cell parameters were obtained. This behaviour is different from that in the RMgSn ternary compounds: the CeScSi is the structure adopted by the heavier lanthanides (starting from Nd to Lu, including Y, but not Sc) while