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Structural peculiarities and electrochemical properties of R_5M_3 (R = La, Gd; M = Ge, Sn) doped by lithium

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Dedicated to Evgen I. Gladyshevskii (1924-2012)

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Ternary phases $R_5Li_xM_3$ were prepared in two ways, by melting and by electrochemical lithiation of the binary compounds R_5M_3. They crystallize in the hexagonal Hf_5CuSn_3 structure type, an ordered superstructure of the Mn_5Si_3 type. Metallic type of bonding was suggested by the analysis of the interatomic distances and confirmed by electronic structure calculations. Electrochemical lithiation reactions of electrodes made of R_5M_3 alloys were studied in an organic electrolyte containing $LiPF_6$ salt, using the conventional charge-discharge technique, and the reaction products were analyzed by X-ray powder diffraction. The partially lithiated phase, $R_5Li_xM_3$ (where $x < 0.4$), appears to be a solid solution of Li in the initial structure of the binary compounds R_5M_3.

Intermetallic compound / Crystal structure / Rare-earth elements / Lithium / Electrochemistry

Introduction

The binary compounds La_5Ge_3 [1], Gd_5Sn_3 [2] and Gd_5Ge_3 [3] crystallize in the hexagonal Mn_5Si_3 structure type [4]. Two polymorphic modifications of La_5Sn_3 are known; the room temperature modification [5] crystallizes in the tetragonal W_5Si_3-type and the high-temperature modification [2] adopts the hexagonal Mn_5Si_3-type. The latter variant of R_5M_3 intermetallics (where R is a rare-earth element and M a main-group element) is characterized by two different sites occupied by R atoms, in Wyckoff positions 4*d* and 6*g*. The M atoms (Ge, Sn or Pb) are located in a second 6*g* site. Binary R_5M_4 and ternary R_5TM_3 phases (T = transition metal) can be formed from R_5M_3 (Mn_5Si_3-type) by incorporation of M or T atoms into an additional site in Wyckoff position 2*b*. The hexagonal Ti_5Ga_4- and Hf_5CuSn_3-types, which are ‘filled’ versions of the Mn_5Si_3-type, are obtained in this case [6].

The new ternary Tb_5LiSn_3 compound, with a fully filled 2*b* site (Hf_5CuSn_3 structure type), was discovered during a systematic study of Tb–Li–Sn alloys [7]. The ternary compound $La_5Li_xGe_3$, formed by incorporation of up to $x = 0.4$ Li atoms into octahedral voids of binary La_5Ge_3, was observed in the La–Li–Ge system [8].

In the present work $R_5Li_xM_3$ samples were prepared in two ways, by melting and by electrochemical lithiation. The effect of Li incorporation on the crystal structure and electrochemical properties of alloys with different rare-earth metals is discussed.

Experimental

Rare-earth (La and Gd), lithium, germanium and tin, all with a nominal purity of more than 99.9 wt.%, were used as starting materials. At the beginning, pieces of pure metals, corresponding to the overall composition $R_{55}Li_{10}M_{35}$, were pressed into pellets, enclosed in tantalum crucibles and placed in a resistance furnace with a thermocouple controller. The samples were heated from ambient temperature to 670 K at a rate of 5 K/min, and kept at this temperature for 2 days. After that, the temperature was increased to 1070 K over 1 h. The alloys were annealed at this temperature for 8 h and then slowly cooled to room temperature. After the melting and annealing procedures, the total weight loss was less than 2 %.

X-ray powder diffraction of the samples was carried out using URD-6 and HZG-4a powder diffractometers (Cu $K\alpha$-radiation). Rietveld refinements of the powder diffraction data were performed with the FullProf program [9].

Electrochemical insertion of lithium into the R_5M_3 binary phases was performed in Swagelok-type cells, which consist of a composite electrode containing 0.2 g alloy mixed with 15 wt.% carbon powder; as counter-electrode pure lithium metal was used. A separator soaked in electrolyte (1M $LiPF_6$ in ethylenecarbonate/dimethylcarbonate, Merck) was placed between the electrodes. The cycling was performed by a galvanostatic cycling procedure with a current rate of 0.1 C.

The electronic structure of the compounds was calculated using the tight-binding linear muffin-tin orbital (TB-LMTO) method in the atomic spheres approximation (TB-LMTO-ASA [10-12]) and experimental crystallographic data reported here. Exchange and correlation were interpreted in the local density approximation [13]. All the figures and graphics concerning electron structure calculations were generated using wxDragon [14].

Results and discussion

The powder diffraction patterns of the $R_{55}Li_{10}Ge_{35}$ and $R_{55}Li_{10}Sn_{35}$ alloys prepared by melting are similar to the powder patterns of the R_5M_3 binary phases, with some minor differences. We decided to examine the powder patterns of these samples more carefully, and refine them by the Rietveld method. The crystallographic data obtained from the refinements (Tables 1 and 2) show that the $R_5Li_xM_3$ compounds crystallize with the hexagonal Hf_5CuSn_3 type of structure (space group $P6_3/mcm$). In the structure of these compounds the lithium atoms occupy the same crystallographic position (2*b*) as the copper atoms in Hf_5CuSn_3. A projection of the unit cell of $Gd_5Li_xSn_3$ (as an example) and the coordination polyhedra of the atoms are shown in Fig. 1. The number of neighboring atoms correlates well with the size of the central atoms. The Gd atoms are enclosed in 14- and 17-vertex polyhedra, whereas the coordination polyhedra of the Sn atoms are pseudo Frank-Kasper polyhedra with CN = 13. The lithium atoms are incorporated into octahedrons with centered facets.

$La_5Li_xGe_3$, $Gd_5Li_xGe_3$ and $Gd_5Li_xSn_3$ limited solid solutions were found along the R_5Ge_3–Li and R_5Sn_3–Li concentration sections. $La_5Li_xGe_3$ and $Gd_5Li_xGe_3$ (x = 0-0.4) solid solutions are formed by incorporation of up to 0.4 lithium atoms per formula unit into the empty octahedrons present in the binary phases. The lattice parameters within the homogeneity range of the solid solutions were determined and refined from powder diffraction data (Table 2). A general tendency to enlargement of the unit cell dimensions with increasing Li content in the structure was observed. A pure $La_5Li_xSn_3$ ternary phase was observed only in the samples with x = 0.4 and 0.5, whereas the alloys with x = 0.1 and 0.2 consisted of two phases: tetragonal binary La_5Sn_3 and hexagonal ternary $La_5Li_xSn_3$.

Table 1 Experimental details and crystallographic data for $R_5Li_xSn_3$.

Starting composition of alloys		$La_{60}Li_5Sn_{35}$	$La_{62}Sn_{38}$	$Gd_{60}Li_5Sn_{35}$	$Gd_{62}Sn_{38}$
Method of lithium incorporation		melting	electrochemical	melting	electrochemical
Composition from X-ray data		$La_{60}Li_6Sn_{34}$	$La_{60}Li_5Sn_{35}$	$Gd_{60}Li_6Sn_{34}$	$Gd_{60}Li_5Sn_{35}$
Formula		$La_5Li_{0.5}Sn_3$	$La_5Li_{0.5}Sn_3$	$Gd_5Li_{0.5}Sn_3$	$Gd_5Li_{0.4}Sn_3$
Diffractometer; radiation		HZG-4a, Cu $K\alpha$	HZG-4a, Cu $K\alpha$	HZG-4a, Cu $K\alpha$	HZG-4a, Cu $K\alpha$
2θ range (deg.), number of points		20÷100, 1601	20÷100, 1601	20÷100, 1601	20÷100, 1601
Step size (deg.), counting time (s)		0.05, 20	0.05, 20	0.05, 20	0.05, 20
Structure type		Hf_5CuSn_3	Mn_5Si_3	Hf_5CuSn_3	Hf_5CuSn_3
Space group		$P6_3/mcm$	$P6_3/mcm$	$P6_3/mcm$	$P6_3/mcm$
Pearson code		*hP*16+1	*hP*16	*hP*16+1	*hP*16+0.8
Unit cell dimensions:					
a (Å)		9.4456(2)	9.4443(3)	9.0458(2)	9.0416(2)
c (Å)		6.9694(2)	6.9677(2)	6.6097(1)	6.6053(1)
Reliability factors:					
R_F (%), R_B (%)		6.21, 7.34	7.11, 9.24	6.34, 7.86	8.34, 9.87
R_p (%), R_{wp} (%)		3.98, 7.09	5.54, 8.03	4.42, 6.49	5.63, 8.43
χ^2		2.86	4.17	3.17	4.56
Atomic parameters (x y z):	$R1$ 4*d*	⅓ ⅔ 0	⅓ ⅔ 0	⅓ ⅔ 0	⅓ ⅔ 0
	$R2$ 6*g*	0.2363(1) 0 ¼	0.2361(2) 0 ¼	0.2371(2) 0 ¼	0.2384(3) 0 ¼
	Sn 6*g*	0.5997(2) 0 ¼	0.5993(3) 0 ¼	0.6001(2) 0 ¼	0.6004(4) 0 ¼
	Li 2*b*	0 0 0		0 0 0	0 0 0

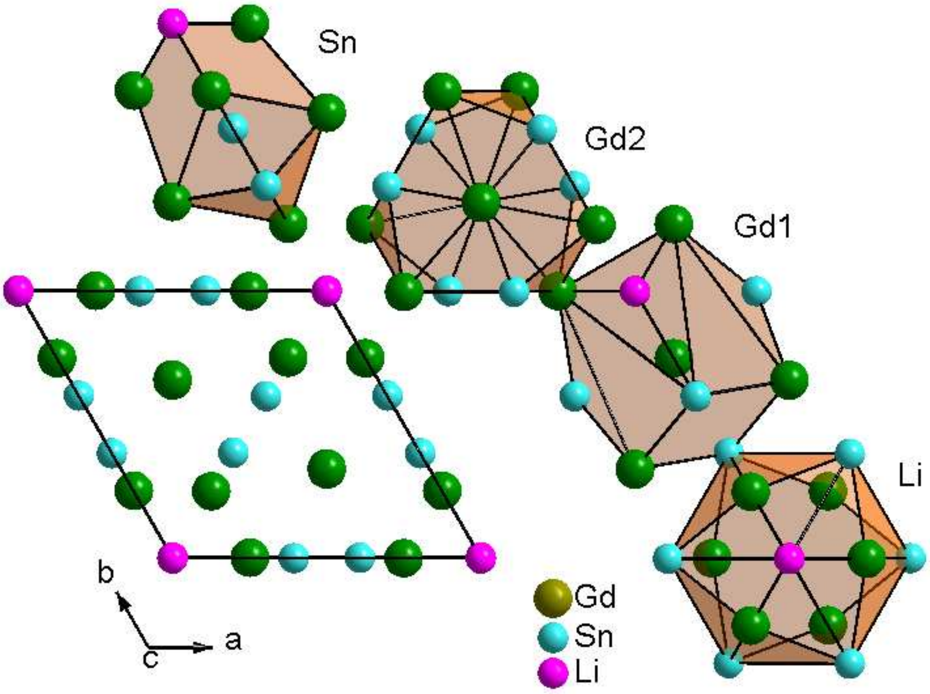

Fig. 1 Projection of the unit cell of $Gd_5Li_{0.4}Sn_3$ and coordination polyhedra of the atoms.

Table 2 Lattice parameters of the R_5M_3 and $R_5Li_xM_3$ phases prepared by melting.

Formula	Prototype, Pearson symbol	Space group	Lattice parameters, Å	
			a	*c*
La_5Ge_3	Mn_5Si_3, *hP*16	$P6_3/mcm$	8.9418(1)	6.8798(1)
$La_5Li_xGe_3$ (x = 0.1)	Hf_5CuSn_3, *hP*18	$P6_3/mcm$	8.9441(1)	6.8820(1)
$La_5Li_xGe_3$ (x = 0.2)	Hf_5CuSn_3, *hP*18	$P6_3/mcm$	8.9476(2)	6.8861(1)
$La_5Li_xGe_3$ (x = 0.3)	Hf_5CuSn_3, *hP*18	$P6_3/mcm$	8.9502(1)	6.9890(1)
$La_5Li_xGe_3$ (x = 0.4)	Hf_5CuSn_3, *hP*18	$P6_3/mcm$	8.9531(2)	6.8921(2)
Gd_5Ge_3	Mn_5Si_3, *hP*16	$P6_3/mcm$	8.5488(1)	6.4391(1)
$Gd_5Li_xGe_3$ (x = 0.1)	Hf_5CuSn_3, *hP*18	$P6_3/mcm$	8.9513(1)	6.4430(1)
$Gd_5Li_xGe_3$ (x = 0.2)	Hf_5CuSn_3, *hP*18	$P6_3/mcm$	8.9539(1)	6.4471(1)
$Gd_5Li_xGe_3$ (x = 0.3)	Hf_5CuSn_3, *hP*18	$P6_3/mcm$	8.9564(2)	6.4506(1)
$Gd_5Li_xGe_3$ (x = 0.4)	Hf_5CuSn_3, *hP*18	$P6_3/mcm$	8.9590(2)	6.4541(2)
La_5Sn_3 (rt)	W_5Si_3, *tI*32	$I4/mcm$	12.748	6.344
La_5Sn_3 (ht)	Mn_5Si_3, *hP*16	$P6_3/mcm$	9.435	6.961
$La_5Li_xSn_3$ (x = 0.4)	Hf_5CuSn_3, *hP*18	$P6_3/mcm$	9.4417(1)	6.9652(1)
$La_5Li_xSn_3$ (x = 0.5)	Hf_5CuSn_3, *hP*18	$P6_3/mcm$	9.4456(2)	6.9694(2)
Gd_5Sn_3	Mn_5Si_3, *hP*16	$P6_3/mcm$	9.0305(1)	6.5942(1)
$Gd_5Li_xSn_3$ (x = 0.1)	Hf_5CuSn_3, *hP*18	$P6_3/mcm$	9.0341(1)	6.5968(1)
$Gd_5Li_xSn_3$ (x = 0.2)	Hf_5CuSn_3, *hP*18	$P6_3/mcm$	9.0376(2)	6.5996(1)
$Gd_5Li_xSn_3$ (x = 0.3)	Hf_5CuSn_3, *hP*18	$P6_3/mcm$	9.0384(1)	6.6021(1)
$Gd_5Li_xSn_3$ (x = 0.4)	Hf_5CuSn_3, *hP*18	$P6_3/mcm$	9.0420(1)	6.6056(1)
$Gd_5Li_xSn_3$ (x = 0.5)	Hf_5CuSn_3, *hP*18	$P6_3/mcm$	9.0458(2)	6.6097(1)

An electronic structure model of Gd_5LiSn_3 with completely filled octahedrons was calculated using the tight-binding linear muffin-tin orbital (TB–LMTO) method in the atomic spheres approximation (TB–LMTO–ASA). The experimental crystallographic data refined here were used for the calculations. As seen from Fig. 2, positive charge density is observed around the Gd atoms and negative charge density is accumulated around the Sn atoms, because the rare-earth and Li atoms donate electrons to the tin atoms. The dominant type of bonding in this compound is metallic. The total density of states (DOS) for Gd_5LiSn_3 (Fig. 2) in the valence band region below the Fermi level, E_F, exhibits significant mixing of Gd and Sn states. In the region above E_F, contributions of *f*- and *d*-orbitals of Gd and *p*-orbitals of Sn are observed. The Sn *s*-type states are mainly located close to the lower valence band (at –8.0 eV). Crystal orbital Hamilton population (COHP) and integrated crystal orbital Hamilton population (iCOHP) calculations were used to make a quantitative evaluation of the bonding strength between the different types of atom. It can be concluded from the COHP data that the strongest interactions in the structure of Gd_5LiSn_3 are between Gd and Sn atoms.

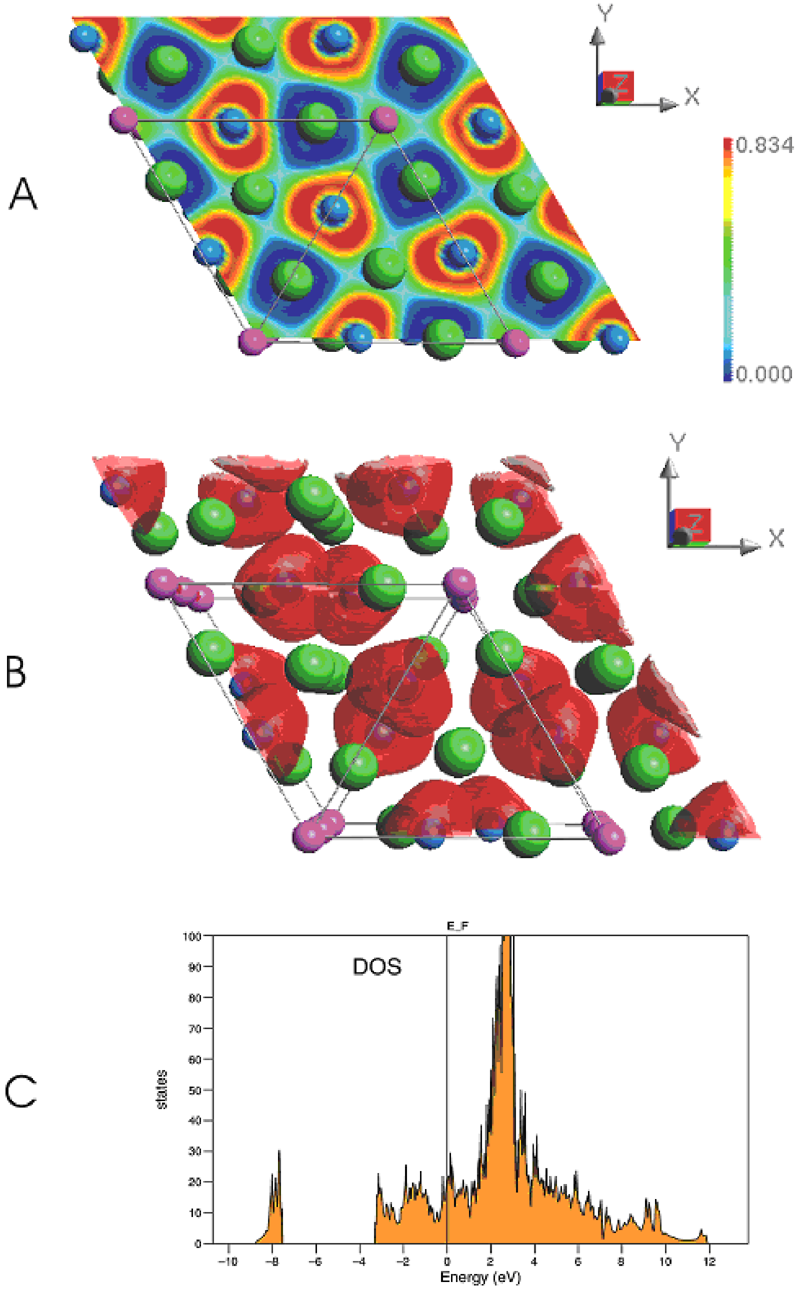

Fig. 2 Electronic localization function (A), isosurfaces (B) and total density of states (C) for ordered Gd_5LiSn_3.

The performance of binary R_5M_3 electrodes in Li-ion batteries was tested in half-cells against metallic lithium as the counter electrode, with 1M $LiPF_6$ in ethylenecarbonate/dimethylcarbonate as standard electrolyte. The voltage profiles for the first and the second cycles (Fig. 3a) show plateaus that confirm the incorporation of lithium into the binary R_5M_3 phases. Reversible Li-insertion was corroborated by the results of cyclic voltammetry. (Fig. 3b). The reversible charge/discharge reaction can be written as:

$$x\text{Li}^+ + R_5M_3 + x\bar{e} \leftrightarrow \text{Li}_xR_5M_3.$$

The anode material was analyzed by X-ray powder diffraction after several charge-discharge cycles (Table 1). The partially lithiated phase, $\text{Li}_xR_5M_3$ (where $x < 0.5$) appears to be a solid solution of Li in the basic crystal structure of the R_5M_3 binary phase. During the lithiation of La_5Sn_3, stabilization of the hexagonal modification was observed.

Acknowledgements

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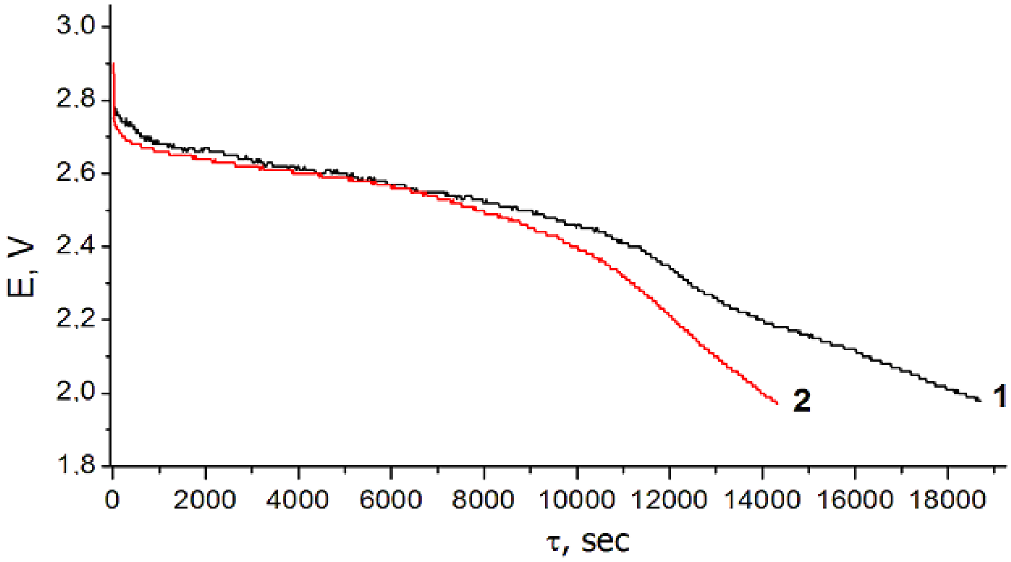
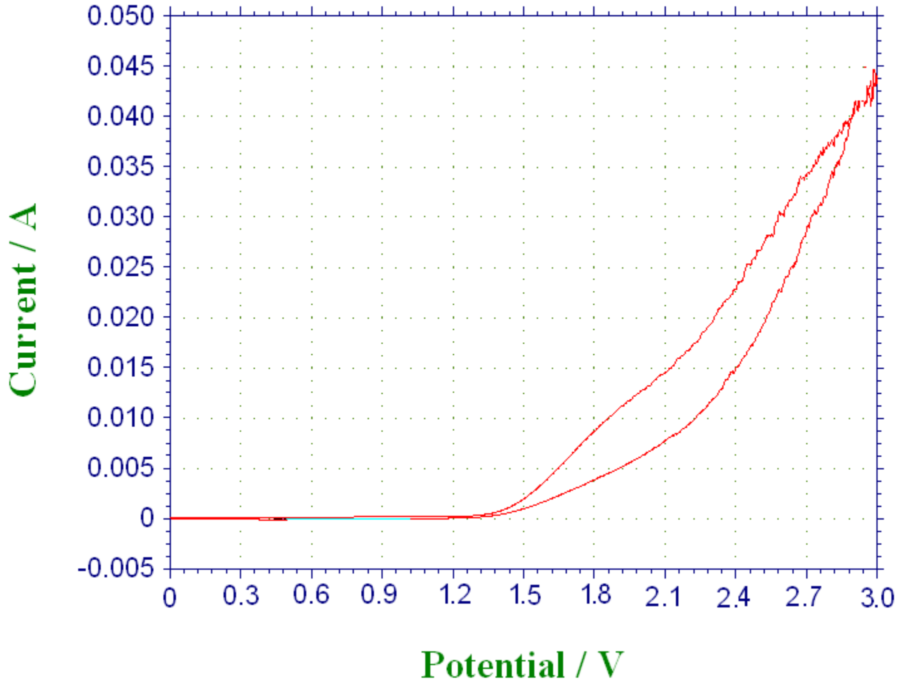


(a)



(b)

Fig. 3 Discharge (a) and cyclic voltammetry (b) plots for $La_5Li_xSn_3$.

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