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Journal of Solid State Chemistry 178 (2005) 2724–2733

JOURNAL OF SOLID STATE CHEMISTRY

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New rare earth metal-rich indides $RE_{14}Ni_3In_3$ (RE = Sc, Y, Gd–Tm, Lu)—synthesis and crystal chemistry

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Received 11 May 2005; received in revised form 13 June 2005; accepted 15 June 2005
Available online 21 July 2005

Abstract

The rare earth–nickel–indides $RE_{14}Ni_3In_3$ (RE = Sc, Y, Gd–Tm, Lu) were synthesized from the elements by arc-melting and subsequent annealing. The compounds were investigated on the basis of X-ray powder and single crystal data: $Lu_{14}Co_2In_3$ type, $P4_2/nmc$, $Z = 4$, $a = 888.1(1)$, $c = 2134.7(4)$, w$R2 = 0.0653$, 1381 F^2 values, 63 variables for $Sc_{13.89}Ni_{3.66}In_{2.45}$; $a = 961.2(1)$, $c = 2316.2(5)$, w$R2 = 0.0633$, 1741 F^2 values, 64 variables for $Y_{13.84}Ni_{3.19}In_{2.97}$; $a = 965.3(1)$, $c = 2330.5(5)$, w$R2 = 0.0620$, 1765 F^2 values, 63 variables for $Gd_{14}Ni_{3.29}In_{2.71}$; $a = 956.8(1)$, $c = 2298.4(5)$, w$R2 = 0.0829$, 1707 F^2 values, 64 variables for $Tb_{13.82}Ni_{3.36}In_{2.82}$; $a = 951.7(1)$, $c = 2289.0(5)$, w$R2 = 0.0838$, 1794 F^2 values, 64 variables for $Dy_{13.60}Ni_{3.34}In_{3.06}$; $a = 948.53(7)$, $c = 2270.6(1)$, w$R2 = 0.1137$, 1191 F^2 values, 64 variables for $Ho_{13.35}Ni_{3.17}In_{3.48}$; $a = 943.5(1)$, $c = 2269.1(5)$, w$R2 = 0.0552$, 1646 F^2 values, 64 variables for $Er_{13.53}Ni_{3.14}In_{3.33}$; $a = 938.42(7)$, $c = 2250.8(1)$, w$R2 = 0.1051$, 1611 F^2 values, 64 variables for $Tm_{13.47}Ni_{3.28}In_{3.25}$; $a = 937.3(1)$, $c = 2249.6(5)$, w$R2 = 0.0692$, 1604 F^2 values, 64 variables for $Tm_{13.80}Ni_{3.49}In_{2.71}$; and $a = 933.4(1)$, $c = 2263.0(5)$, w$R2 = 0.0709$, 1603 F^2 values, 64 variables for $Lu_{13.94}Ni_{3.07}In_{2.99}$. The $RE_{14}Ni_3In_3$ indides show significant Ni/In mixing on the 4c In1 site. Except the gadolinium compound, the $RE_{14}Ni_3In_3$ intermetallics also reveal RE/In mixing on the 4c RE1 site, leading to the refined compositions. Due to the high rare earth metal content, the seven crystallographically independent RE sites have between 9 and 10 nearest RE neighbors. The $RE_{14}Ni_3In_3$ structures can be described as a complex intergrowth of rare earth-based polyhedra. Both nickel sites have a distorted trigonal-prismatic rare earth coordination. An interesting feature is the In2–In2 dumb-bell at an In2–In2 distance of 304 pm (for $Gd_{14}Ni_{3.29}In_{2.71}$). The crystal chemical peculiarities of the $RE_{14}Ni_3In_3$ indides are briefly discussed.

Keywords: Intermetallic compounds; Crystal structure; Indium

1. Introduction

Ternary rare earth (RE)–transition metal (T)–indides $RE_xT_yIn_z$ display a peculiar crystal chemistry [1]. If x, y, and z have almost similar values, the transition metal and indium atoms build up two- or three-dimensional $[T_yIn_z]$ polyanionic networks in which the rare earth atoms fill cages or channels. If the indium content of such intermetallics is significantly increased, the structural building principle remains almost the same, however, the indium atoms build up indium substructures within the three-dimensional $[T_yIn_z]$ polyanions

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doi:10.1016/j.jssc.2005.06.021

which resemble the elemental indium structure, i.e. distorted indium cubes. An overview of these substructures is given in [1–3].

The situation is different, if the transition metal or the rare earth metal contents are very high. In the case of *T*-rich indides, the transition metal atoms show different kinds of one-, two-, or three-dimensional *T*-clusters. Interesting examples are the structures of $LaNi_2In$, $CeNi_4In$, $Ce_4Ni_7In_8$, and $LaNi_7In_6$ [4]. With a high rare earth metal content, there exist only few structural series of such compounds: $RE_{12}Ni_6In$ (RE = Y, La, Pr, Nd, Sm, Gd) and $RE_{12}Co_6In$ (RE = La, Pr, Nd, Sm) with $Sm_{12}Ni_6In$ type [5–7], RE_6Co_2In (RE = Y, Sm, Gd–Ho, Tm, Lu) with Ho_6Co_2Ga structure [7,8], $RE_{14}Co_2In_3$ (RE = Y, Gd–Tm, Lu) [9] with $Lu_{14}Co_2In_3$ type, Er_5Ni_2In and $Tm_{4.83(3)}Ni_2In_{1.17(3)}$ [10] with Mo_5SiB_2 structure, and the series $RE_{12}Pt_7In$ (RE = Ce, Pr, Nd, Gd, Ho) [11] with an ordered version of the Gd_3Ga_2 type. All these intermetallics have high coordination numbers and chemical bonding is significantly governed by the many *RE*–*RE* contacts. The structures can be described by a complex packing pattern of different polyhedra [6,7].

Recently Canepa et al. [12] reported a single crystal study of the gadolinium-based indide $Gd_{14}Co_3In_{2.7}$. The latter compound is related to the $Lu_{14}Co_2In_3$ type indides, however, the gadolinium compound shows an additional 4*d* Co2 site, defects on the 8*g* Co1 site, and a mixed Co/In occupancy on the 4*c* site. During our systematic phase analytical studies of the *RE*–Ni–In systems [4,13–19], we found a family of new nickel compounds $RE_{14}Ni_3In_3$ (RE = Sc, Y, Gd–Tm, Lu), which form only with the smaller rare earth elements. These indides also show an additional 4*d* Ni2 site, similar to $Gd_{14}Co_3In_{2.7}$ [12], but also some *RE*/In mixing of the 4*c* *RE*1 sites. The synthesis, crystal growth, structure determination and crystal chemistry of these phases are reported herein. A preliminary account of some of this work was given recently at a conference [20].

Besides the structural chemistry described herein, the main interest in such materials concerns their magnetic and electrical properties. Especially the gadolinium-based materials are promising candidates for magnetic refrigeration devices, e.g. the isotypic cobalt compound $Gd_{14}Co_3In_{2.7}$ [12] was investigated along that line.

2. Experimental

2.1. Synthesis

Starting materials for the preparation of the $RE_{14}Ni_3In_3$ intermetallics with RE = Sc, Y, Gd–Tm, Lu) were ingots of the rare earth elements (Chempur, Johnson Matthey, or Kelpin), nickel wire (∅ 0.38 mm, Johnson-Matthey) or nickel powder (Johnson-Matthey), and indium tear drops (Johnson-Matthey), all with stated purities better than 99.9%. All samples were prepared directly from the elements via arc-melting [21] under an atmosphere of ca. 600 mbar argon. The argon was purified before over titanium sponge (900 K), silica gel, and molecular sieves. Except the thulium-based compounds, the elements were weighed in the ideal 14:3:3 atomic ratios. Two samples with thulium were prepared with the starting compositions Tm:Ni:In of 66:29:5 and 67:22:11. All samples were turned over and remelted two times in the arc-melting crucible in order to achieve homogeneity. The weight losses were always smaller than 0.5 wt%.

The $RE_{14}Ni_3In_3$ indides were obtained only in polycrystalline form after the arc-melting procedures. These samples were then sealed in tantalum tubes under an argon pressure of ca. 800 mbar. The tantalum ampoules were subsequently enclosed in evacuated silica ampoules for oxidation protection and the samples were heated in a box furnace at 1270 K for 3 h, then cooled at a rate of 5 K/h to 870 K and held at that temperature for 24 h. Finally the samples were cooled to room temperature within 3 h. This procedure led to the formation of crystals, suitable for intensity data collections. The silvery brittle samples were stable in moist air over months. Powders of the $RE_{14}Ni_3In_3$ indides are dark gray. Single crystals exhibit metallic luster.

2.2. X-ray powder diffraction and scanning electron microscopy

All samples were investigated by Guinier powder diffraction (imaging plate technique, Fujifilm BAS-1800) with Cu $K\alpha_1$ radiation and α-quartz ($a = 491.30$, $c = 540.46$ pm) as an internal standard. The tetragonal lattice parameters (Table 1) were obtained from least-squares fits of the Guinier data. The indexing of the complex powder patterns was facilitated through intensity calculations [22] using the positional parameters of the structure refinements.

The crystals investigated on the diffractometers have been analyzed in a scanning electron microscope (LEICA 420i) through energy dispersive analyses of X-rays. The rare earth trifluorides, nickel metal, and InAs were used as standards. No impurity elements heavier than sodium have been observed. The experimentally determined compositions were close to the compositions calculated from the structure refinements. To give an example, the scandium-containing crystal had a refined composition of 69.5 at% Sc:18.3 at% Ni:12.2 at% In, as compared to the EDX data of 70 ± 1 at% Sc:17 ± 1 at% Ni:13 ± 1 at% In. The standard uncertainty accounts for the various point measurements.