2520 *Chem. Mater.* **2000,** *12,* 2520−2522

Molten Ga as a Solvent for Exploratory Synthesis: The New Ternary Polygallide Sm_2NiGa_{12}

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Received March 14, 2000
Revised Manuscript Received July 11, 2000

Recently we began investigating molten Al and Ga as potential solvents for the systematic exploratory synthesis of silicides, germanides, and related compounds. We reported that $RE_2Al_3Si_2$ (RE = Y, Dy, Ho, Tm, Er),[1] $Sm_2Ni(Si_{1-x},Ni_x)Al_4Si_6$,[2] and $RENiAl_4Ge_2$ (RE = Sm, Tb, Y)[3] form readily in solutions of molten Al. In these reactions a solution of Si or Ge is formed in liquid Al which becomes available for reaction with other elements (e.g., rare earths, transition metals) to form ternary or quaternary compounds. To assess the behavior of liquid Ga vis à vis Al, we performed corresponding experiments using Ga as a solvent and observed substantially different chemical reactivity. Namely, Al analogues of the quaternary compounds $Sm_2Ni(Si_{1-x},Ni_x)Al_4Si_6$ did not form. In the case of Sm/Ni/Si/Ga phase separation occurred to give $SmNiSi_3$,[4] and the new compound Sm_2NiGa_{12}. The latter exhibits an interesting tetragonal structure with a fascinating three-dimensional (3D) network. Here we report the synthesis, structure, and properties of Sm_2NiGa_{12}. It is noteworthy to mention that many RE/Ni/Ga phases exist[5] and the Sm/Ni/Ga phase diagram already contains a striking number of phases namely, SmNiGa, $SmNiGa_2$, Sm_2Ni_2Ga, $SmNi_3Ga_2$, $Sm_3Ni_6Ga_2$, $SmNiGa_3$, Sm_2NiGa_3, $SmNiGa_4$, $Sm_{26}Ni_{11}Ga_6$, Sm_4NiGa_7, and $Sm_{17}Ni_{58}Ga_{25}$.[6] None of these materials was synthesized in Ga flux. It is rather remarkable that despite the great number of ternary compounds in this system Sm_2NiGa_{12} is yet a new addition.

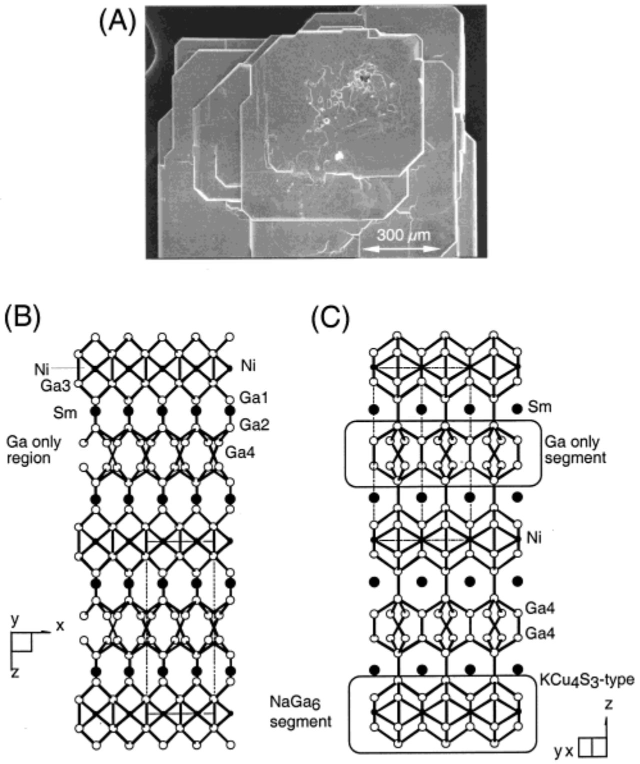

Figure 1. (A) Typical crystals of Sm_2NiGa_{12} grown from Ga solution. (B) and (C) Two views of the structure of Sm_2NiGa_{12} with atomic labeling. The two different segments are indicated.

Sm_2NiGa_{12} was originally discovered from the reaction of Sm, Ni, and Si carried out in excess Ga at 900 °C for 4 days.[7] Subsequently, it was prepared as a single phase by dissolving Sm and Ni in a 2:1 ratio in ∼20 equiv of Ga at 800 °C. The compound forms square-shaped plates that possess a gray metallic sheen (see Figure 1A). Occasionally, the pseudo-quaternary Sm/Ni/Ga/Si phase was obtained as a byproduct, among well-formed crystals of $SmNiSi_3$, which turned out to be the isostrucutral $Sm_2NiGa_{12-x}Si_x$ ($x \approx 0.25$).[8] The presence of Si and the value of x were determined with EDS microprobe analysis as well as careful refinement of the single crystal X-ray crystallographic data. Only the site of Ga(4) was found to contain Si (see below).

Sm_2NiGa_{12} adopts a tetragonal structure[9] which has not been noted for other RE/Ni/Ga or RE/Ni/Al systems.

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(7) Sm_2NiGa_{12} was synthesized by the reaction of Sm (1.33 mmol) and Ni (0.68 mmol), in Ga (12.20 mmol). The mixture was placed inside an alumina tube which was flame-sealed inside a silica tube under vacuum (∼10^{-4} Torr). The tube was heated to 900 °C over 12 h, kept at 900 °C for 96 h, then cooled to 300 °C at 8.3 °C/h, and to 50 °C at 125 °C/h. The excess gallium flux was removed by first placing the alumina tube in boiling deionized water for about 20 min. The alumina tube and the water were removed, and the remaining solid material was washed with three aliquots of acetone. The solid material was placed into about 50 mL of 5% (v/v) bromine in *N*,*N*-dimethylformamide (DMF) solution for 2 days. After the bromine solution was decanted, the product was washed with three aliquots of DMF, three aliquots of acetone, and three aliquots of ether. Shiny, silver square plates and chunks were obtained, yield ∼88% based on Ni. Powder X-ray diffraction indicated only one phase. Energy dispersive spectroscopy (EDS) on several single crystals gave "Sm_2NiGa_{11}". The crystals are air and water stable and can resist aqua regia up to 24 h.

10.1021/cm0002261 CCC: $19.00

It can be described as a 3D framework of [$NiGa_{12}$] with Sm atoms residing in cavities made of Ga atoms (Figure 1B). The [$NiGa_{12}$] part of the structure can be separated into two distinct alternating two-dimensional segments: a $NiGa_6$ segment and a Ga-only segment. The $NiGa_6$ segment, shown in Figure 1B has a similar structure to the [$NiAl_4Si_2$] fragment found in $Sm_2Ni(Si_{1-x},Ni_x)Al_4Si_6$[2] and it is reminiscent of the KCu_4S_3 structure type. The $NiGa_6$ section is also similar to that of $LaGa_6Ni_{1-x}$[6] and $Ce_4Ni_2Ga_{17}$.[10] The Ni atoms are found in an almost cubic environment of eight Ga atoms with a Ni−Ga distance of 2.480(1) Å.

The two-dimensional Ga-only network segment possesses Ga−Ga bonds ranging from 2.548(1) to 2.594(1) Å. The next shortest distances are found at 2.949(2) Å which may represent weak Ga···Ga interactions. This Ga-only layer is connected to the $NiGa_6$ segment via Ga−Ga bonds at 2.419(1) Å which are the shortest in the structure. Interestingly, if all Sm and Ni atoms are removed from the structure, we still see a continuous 3D Ga framework in which the Ga atoms are connected via bonds ranging from 2.419(2) to 2.611(2) Å. At a bonding cutoff distance of ~3.3 Å, the coordination number of the Sm atoms in the structure is 12.

To gain deeper insight into the bonding and properties of Sm_2NiGa_{12}, band structure calculations were performed, at the extended Hückel tight-binding theory level,[11] using Y to mimic the Sm.[12] The calculated electronic band structure predicts the compound to be a metallic conductor. The total density of states (DOS) is shown in Figure 2. The region around −14 eV is contains a set of weakly dispersed bands located close to the ionization potential of the Ni 3d orbitals. The major peak, ranging from −14.8 to −13.5 eV, corresponds to the d orbital manifold of Ni. Below −14.8 eV, a series of very dispersed bands consist primarily of Ga 4s orbitals weakly hybridized with the Y 5s and Ni 4s orbitals. The band structure, between −13.5 eV and the Fermi level, is dominated by the Ga 4p orbitals feebly mixed with the Ni 4s and the Y 4d orbitals. The latter indicates a certain extent of back charge transfer from the Ga atoms to the rare earth atoms to partially fill their 4d orbitals. Surprisingly, above the Fermi level the bands mainly derive from an almost equal contribution from Ga 4p and Y 4d orbitals. This strong Ga−Y hybridization, above the Fermi level, makes this compound very different from the silicides[2,4] but similar to the other gallides.[13] Therefore, the rare earth element acts not only as an electron donor to the [$NiGa_{12}$] framework but also participates in strong covalent bonding with it.

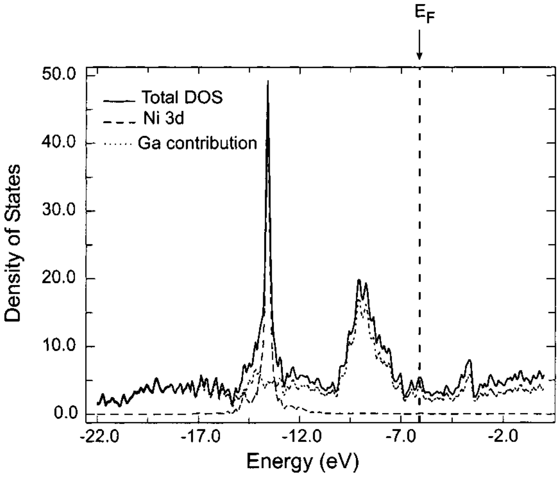

Figure 2. Total DOS for the Y_2NiGa_{12} and partial DOS corresponding to the Ni 3d orbitals and to the Ga contributions. The Fermi level is drawn with dashed line.

On the basis of the DOS plots the Ni d as well as s orbitals are filled, resulting in a reduced state approaching a diamagnetic $d^{10}s^2$ configuration. This can be understood by the fact that Ni is actually the most electronegative element in the structure.[14] Therefore,

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(8) (a) The pseudo-quaternary phase $Sm_2NiGa_{12-x}Si_x$ ($x \approx 0.4$) was obtained as a byproduct in the reactions performed in the Sm/Ni/Si/Ga system. $Sm_2NiGa_{12-x}Si_x$ crystals were recovered from the reaction of Sm (2.4 mmol), Ni (1.2 mmol), and Si (8.4 mmol) in Ga flux (24.4 mmol). The reaction was carried out in an alumina crucible sealed in a fused silica tube under vacuum. The samples were heated at a rate of 60 °C/h to 1000 °C, left at 1000 °C for 5 h to allow proper melting and homogenization, quickly brought down to 850 °C, kept there for 10 days, and slowly cooled to 150 °C at 6 °C/h. The product was isolated from the Ga flux by treating it with ~1 M solution of I_2 in DMF at 60 °C for 5 h and at room temperature for 24 h. (b) $Sm_2NiGa_{12-x}Si_x$. Crystal data: A Bruker Smart CCD diffractometer equipped with a graphite crystal monochromator and Mo Kα ($\lambda = 0.71096$ Å) radiation was used to collect data from a crystal of dimensions 0.05 × 0.05 × 0.01 mm. The data were extracted using the SAINT software package. The structure was solved and refined with full-matrix least-squares techniques with the SHELX software package. Crystal data at 293 K: $a = 5.9855(1)$ Å, $c = 15.404(6)$ Å; $\alpha = \beta = \gamma = 90°$; $V = 551.9(3)$ Å^3; $Z = 2$; $d_{calc} = 7.134$ g/cm^3; space group $P\,4/nbm$; μ(Mo Kα) = 4.067 cm^{-1}; $2\theta_{max} = 57°$; octants collected $-7 \le h \le 7, -7 \le k \le -7, -13 \le l \le 20$; number of total data collected is 3001; number of unique data 384 ($R_{int} = 0.0723$); number of variables 27. An absorption correction was made with SADABS. All atoms were refined anisotropically. The final $R/R_w = 0.047/0.129$. The Si atom was located only in the Ga(4) position.

(9) Sm_2NiGa_{12}: A Bruker Smart CCD diffractometer equipped with a graphite crystal monochromator and Mo Kα ($\lambda = 0.71096$ Å) radiation was used to collect data from a crystal of dimensions 0.24 × 0.24 × 0.03 mm. The structure was solved using the TEXSAN software package and refined using the full-matrix least-squares techniques. Crystal data at 293 K: $a = 5.9953(3)$ Å, $c = 15.401(1)$ Å; $\alpha = \beta = \gamma = 90°$; $V = 553.57(6)$ Å^3; $Z = 2$; $d_{calc} = 7.176$ g cm^{-3}; space group $P4/nbm$ (no. 124); μ(Mo Kα) = 4.067 cm^{-1}; $2\theta_{max} = 56.52°$; octants collected $-7 \le h \le 7, -7 \le k \le 7, -18 \le l \le 20$; number of total data collected is 5768; number of unique data is 392 ($R_{int} = 0.0695$); number of data with $F_o^2 > 3\sigma(F_o^2)$ is 392; number of variables 26. An empirical absorption correction using ψ scans was performed. All atoms were refined anisotropically. The final $R/R_w = 0.0654/0.1876$. Fractional atomic coordinates and equivalent isotropic displacement parameters (×10^3) (U_{eq}): Sm $^3/_4$, $^1/_4$, 0.2450(1), 7(1); Ga(1) $^3/_4$, $^3/_4$, 0.1811(3), 10(1); Ga(2) $^3/_4$, $^3/_4$, 0.3394(2), 10(1); Ga(3) 0.5074(4), 0.0074(4), −0.0833(2), 17(1); Ga(4) 0.5720(4), 0.0720(4), 0.4279(2), 16(1); Ni $^3/_4$, $^1/_4$, 0, 20(2).

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(12) (a) Nordell, K. J.; Miller, G. J. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2008−2010. (b) The use of Y atoms is intended to avoid including the incomplete f shell of rare elements in the calculations.

(13) Calculations on $RENi_3Ga_9$ compounds: Small, P.; Sportouch, S.; Kanatzidis, M. G. Work in progress.

(14) Pauling electronegativity scale.

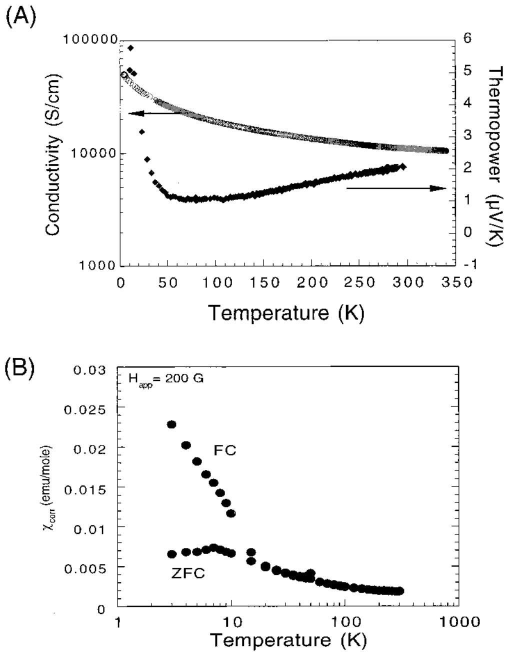

Figure 3. (A) Electrical conductivity and thermopower data of a pressed pellet sample of Sm_2NiGa_{12} as a function of temperature. (B) Molar magnetic susceptibility as a function of temperature for Sm_2NiGa_{12}. The susceptibility was corrected for diamagnetic contributions only. Applied field: 200 G.

electron density tends to flow to Ni from both the rare earth and Ga atoms. This points to an effective reduction of the Ni atoms and implies that the compound is as much as a “nickelide” as it is a gallide. The charge distribution in the Ga substructure suggests that Ga(1) and Ga(2) are slightly reduced (electron density: 3.2682 and 3.3354, respectively). This may be attributed to the close proximity of Y atoms which transfer electron density to their immediate neighbors Ga(1) and Ga(2). On the other hand Ga(3) and Ga(4) are suggested to be nearly neutral.

The electrical resistivity and thermopower data obtained from Sm_2NiGa_{12} indicate highly metallic p-type behavior, in accordance with the predictions of electronic band structure calculations. The resistivity at room temperature is very low at $\sim 95\ \mu\Omega$ cm (conductivity $\sim$10 500 S/cm), and it exhibits a typical metallic temperature dependence (see Figure 3A). The corresponding thermopower is very small at $\sim +3\ \mu$V/K and decreases with temperature down to $\sim$65 K (see Figure 3B). Below this temperature an increase is observed which is attributed to phonon-drag effects[15] typically encountered in good metals.

The susceptibility of Sm_2NiGa_{12} shows an antiferromagnetic ordering with a maximum at $\sim$9 K with irreversibility in the field cooled (FC) and zero-field cooled (ZFC) data which becomes evident below 14 K, see Figure 3B. The material seems to follow Curie–Weiss law above 12 K only after accounting for a large temperature-independent Pauli paramagnetism of $\sim 8.6 \times 10^{-4}$ emu/mol. From the linear portion of the data the slope gives a μ_{eff} of 0.54 μ_B per Sm atom which is consistent with a Sm^{3+} center. The low magnetic moment can be fully accounted by the Sm^{3+} atoms and thus the Ni atoms appear to be diamagnetic in accordance with their reduced state suggested by the electronic structure calculations.

The facile synthesis of Sm_2NiGa_{12} from molten Ga as the solvent, in a ternary system with an existing plethora of phases, underscores the great potential of this synthetic approach to the exploratory synthesis of new intermetallics. Additional isostructural members such as Ce_2NiGa_{12}, Pr_2NiGa_{12}, and Nd_2NiGa_{12} have also been similarly prepared.

Acknowledgment. Financial support from the Department of Energy (Grant DE-FG02-99ER45793) is gratefully acknowledged. We thank M. H. Whangbo for use of his CAESAR software package.

Supporting Information Available: Crystallographic data, fractional atomic coordinates, anisotropic displacement parameters, and bond distances and angles for Sm_2NiGa_{12} and $Sm_2NiGa_{12-x}Si_x$. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) Phonon-drag effects are often seen in many metal systems such as Au, Ag, and Cu. These effects are not due to a transition, and they are not observed in the corresponding electrical resistivity data. See for example: *Thermoelectricity in Metallic Conductors*; Blatt, F. J., Schroeder P. A., Eds.; Plenum Press: New York, 1977.