Journal of Solid State Chemistry 196 (2012) 409–415

Contents lists available at SciVerse ScienceDirect

Journal of Solid State Chemistry

journal homepage: www.elsevier.com/locate/jssc

Rare-earth chromium gallides RE_4CrGa_{12} (RE=Tb–Tm)

Brianna R. Slater [a], Haiying Bie [a], Stanislav S. Stoyko [a], Eric D. Bauer [b], Joe D. Thompson [b], Arthur Mar [a,*]

[a] Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada T6G 2G2
[b] Materials Physics and Applications Division, Los Alamos National Laboratory, Los Alamos, NM 87545, USA

ARTICLE INFO

Article history:
Received 6 April 2012
Received in revised form
12 June 2012
Accepted 4 July 2012
Available online 13 July 2012

Keywords:
Rare-earth metals
Chromium
Gallium
Intermetallic phases
Magnetic properties
Electronic structure

ABSTRACT

The ternary rare-earth-metal chromium gallides RE_4CrGa_{12} (RE=Tb–Tm) have been prepared by reactions of the elements at 1000 °C in the presence of excess gallium used as a self-flux. Their structures are derived by inserting Cr atoms into a quarter of the empty Ga_6 octahedral clusters found in the parent binary gallides REGa$_3$ ($AuCu_3$-type), although single-crystal X-ray diffraction studies suggest that complex superstructures may be adopted. An ideal ordered Y_4PdGa_{12}-type structure was successfully refined for a crystal of Dy_4CrGa_{12} (Pearson symbol $cI34$, space group $Im\overline{3}m$, Z=2, a=8.572(1) Å). Magnetic measurements on single-crystal samples reveal ferromagnetic or possibly ferrimagnetic ordering for the Tb, Dy, and Er members (T_C=22, 15, and 2.8 K, respectively) and antiferromagnetic ordering for the Ho member (T_N=7.5 K). Band structure calculations on a hypothetical "Y_4CrGa_{12}" model suggest that the Cr atoms carry no local magnetic moment.

1. Introduction

Binary rare-earth-metal trigallides REGa$_3$ with the cubic $AuCu_3$-type structure are known for RE=Sc, Tb–Tm, Lu, U, and Np [1–5]. This simple structure, with RE atoms at the corners and Ga atoms at the face centers of the cubic unit cell, features a vacant octahedral site at the body center that is ~2.1 Å (half the cell length) distant from the surrounding Ga atoms. The interstitial site can be filled to various degrees by guest atoms M. Full occupation to give a perovskite ($CaTiO_3$-type) structure with the formulation REMGa$_3$ has not been observed, although the inverse structures RE_3GaX (X=C, N) are known [6,7]. Half occupation to give a K_2PtCl_6-type structure is found in RE_2MnGa_6 [8]. By far the most common scenario is quarter occupation to give a Y_4PdGa_{12}-type structure, which forms for RE_4MGa_{12} (M=Fe, Ni, Pd, Pt, Ag) [9–14] as well as the uranium analogs U_4MGa_{12} (M=Fe, Co, Rh, Ni, Pd) [15–18] and quaternary mixed gallide-germanides $RE_4M_{1-x}Ga_{12-y}Ge_y$ (M=Mn, Fe) [19,20]. It may also be possible for the occupation to vary continuously, as suggested by the homogeneity range of x=0–0.3 in $TmMn_xGa_3$ [21].

The primary interest in the quarter-occupied gallides RE_4MGa_{12} and related compounds rests in their magnetic properties. Most representatives whose magnetic properties have been measured (largely the M=Fe, Pd, and Pt members) display antiferromagnetic ordering [11,12,14,19]. The effective magnetic moments appear to have no contributions from the transition-metal atoms M, implying that they form completely filled d-bands well below the Fermi level. Ferromagnetic ordering can be induced through substitution with an earlier transition metal, which is more likely to give partially filled d-bands crossed by the Fermi level, as shown in $Y_4Mn_{1-x}Ga_{12-y}Ge_y$, whose Curie temperature can be modified through doping [20].

In the course of investigating ternary gallide systems RE–M–Ga containing earlier transition metals, we have identified the series RE_4CrGa_{12} (RE=Tb–Tm). We report here their crystal growth and magnetic properties, and discuss their bonding and electronic structure analyzed through band structure calculations.

2. Experimental

2.1. Synthesis

Starting materials were RE pieces (99.9%, Hefa), Cr powder (99%, Alfa-Aesar), and Ga pieces (99.99%, Cerac). Substitutional reactions with different RE metals established that RE_4CrGa_{12} forms for RE=Tb–Tm but not for RE=Y, Sm, Gd, Yb, and Lu. Although arc-melting of stoichiometric mixtures (4 RE+Cr+12 Ga) followed by annealing at 1000 °C over 2 weeks was attempted, no suitable single crystals could be obtained from this method and the products were not single-phase. Because the ternary gallides RE_4CrGa_{12} possess a crystal structure derived from that of the binary gallides REGa$_3$, their powder X-ray diffraction patterns are very similar. Moreover, crystals of

* Corresponding author. Fax: +1 780 492 8231.
E-mail address: arthur.mar@ualberta.ca (A. Mar).

0022-4596/$ - see front matter © 2012 Elsevier Inc. All rights reserved.
http://dx.doi.org/10.1016/j.jssc.2012.07.009

REGa$_3$ and RE_4CrGa$_{12}$ are indistinguishable in their cubic habits. It is thus especially important to characterize RE_4CrGa$_{12}$ in the form of single-crystal samples. In lieu of the arc-melting procedure, the elements were reacted directly in the presence of excess Ga acting as a self-flux (4 RE+Cr+30 Ga), in alumina crucibles placed within fused-silica tubes which were then evacuated and sealed. The tubes were heated at 1000 °C for 7 h, cooled to 850 °C over 2 h, and cooled to 250 °C over 50 h. At this point, the tubes were removed from the furnace and centrifuged to spin off the Ga flux from the product. Any remaining flux was removed by sonication in ethanol followed by treatment with 3 M I_2 in DMF over 12 h. This procedure yielded small crystals (typically <0.5 mm in their longest dimensions) (Fig. S1 in Supplementary Data) from which specimens were selected for single-crystal X-ray diffraction analysis. Energy-dispersive X-ray (EDX) analysis on these crystals on a Zeiss EVO MA 15 or a JEOL JSM-6010LA scanning electron microscope confirmed the presence of all three elements in proportions (26(2)% RE, 4(2)% Cr, 70(3)% Ga) that agree well with expectations (24% RE, 6% Cr, 70% Ga). To obtain larger crystals for magnetic measurements, the syntheses were repeated as before except that the tubes were held at 850 °C for 7 h and cooled to 250 °C over 84 h. The slower cooling rate yielded larger crystals (>0.5 mm) confirmed by EDX analysis to have uniform composition (Fig. S2 in Supplementary Data). These crystals were generally fractured and thus unsuitable for single-crystal diffraction analysis, but they were adequate for magnetic measurements, after which they were analyzed by powder X-ray diffraction (vide infra).

2.2. Structure determination

Single crystals of RE_4CrGa$_{12}$ were selected only after they were confirmed by EDX analysis to be the ternary compounds and not binary gallides for which they are easily mistaken by visual inspection alone. Intensity data were collected at 295 K on a Bruker Platform/SMART 1000 or a Bruker D8/SMART APEX II diffractometer equipped with Mo $K\alpha$ radiation source. Face-indexed numerical absorption corrections were applied. Structure solution and refinement were carried out with use of the SHELXTL (version 6.12) program package [22].

Numerous crystals examined revealed intense reflections corresponding to a ~4 Å cubic subcell and weaker reflections indexed to ~17 Å cubic supercell (Fig. S3 in Supplementary Data). In the subcell, a structural model with the formulation "RECr$_{0.25}$Ga$_3$" in space group $Pm\overline{3}m$ (no. 221) can be proposed with RE in 1b (½, ½, ½), quarter-occupied Cr in 1a (0, 0, 0), and Ga in 3d (½, 0, 0). Although this model gave satisfactory residuals ($R(F)<0.05$), the Cr sites are coordinated octahedrally by Ga atoms at unphysically short distances of 2.1–2.2 Å. This could be corrected by introducing deficiencies in the Ga sites and allowing the Cr occupancy to vary (i.e., "RECr$_x$Ga$_{3-y}$"), but we note the good agreement of the EDX analyses to the ideal formulation RE_4MGa$_{12}$ which is generally found for other transition-metal substituents M. Any model proposed in the cubic subcell must necessarily place symmetry-equivalent Cr atoms in the centers of all Ga$_6$ octahedra, which are linked by corner-sharing, and no amount of distortion in these octahedra can alleviate the unphysically short Cr–Ga distances.

Transformation to larger supercells, either by doubling to $a=\sim 8$ Å or quadrupling to $a=\sim 17$ Å, permits multiple Cr sites to be introduced in the structural models with more reasonable 2.4–2.5 Å distances to surrounding Ga atoms. Unfortunately, the difference electron density maps invariably revealed additional Cr sites that suffered from the same short Cr–Ga distances, and we were unable to improve the refinements much further ($R(F)>0.15$ with substantial remaining difference electron density), whatever cubic space group was attempted. There is now emerging evidence in the literature that related RE_4MGa$_{12}$ compounds can exhibit highly complex modulated structures associated with long-range ordering of M vacancies [20]. In effect, REGa$_3$ and RE_4MGa$_{12}$ can easily form

Table 1
Comparison of cell parameters for RE_4CrGa$_{12}$ and REGa$_3$ (RE=Tb–Tm) [a].

	Tb$_4$CrGa$_{12}$	Dy$_4$CrGa$_{12}$	Ho$_4$CrGa$_{12}$	Er$_4$CrGa$_{12}$	Tm$_4$CrGa$_{12}$
a (Å)	17.126(2)	17.072(1)	17.120(1)	16.964(1)	16.894(1)
a/4 (Å)	4.282(1)	4.268(1)	4.280(1)	4.241(1)	4.224(1)
V (Å^3)	5023(2)	4975(1)	5018(1)	4882(1)	4822(1)
V/64 (Å^3)	78.48(3)	77.74(1)	78.40(2)	76.28(1)	75.34(2)
	TbGa$_3$	DyGa$_3$	HoGa$_3$	ErGa$_3$	TmGa$_3$
a (Å)	4.285(1)	4.271(1)	4.235(1)	4.219(1)	4.202(1)
V (Å^3)	78.68(5)	77.91(5)	75.96(5)	75.10(5)	74.19(5)

[a] Cell parameters for REGa$_3$, obtained from powder XRD data for RE=Tb, Dy, Er, Tm and single-crystal data for RE=Ho, are taken from Ref. [2].

Table 2
Crystallographic data for Dy$_4$CrGa$_{12}$.

Data collection and refinement	
Formula	Dy$_4$CrGa$_{12}$
Formula mass (amu)	1538.64
Space group	$Im\overline{3}m$ (No. 229)
a (Å)	8.572(1)
V (Å^3)	629.9(2)
Z	2
ρ_{calcd} (g cm^{-3})	8.113
T (K)	295(2)
Crystal dimensions (mm)	0.11 × 0.06 × 0.06
Radiation	Graphite monochromated Mo $K\alpha$, λ=0.71073 Å
μ(Mo $K\alpha$) (mm^{-1})	49.34
Transmission factors	0.042–0.154
2θ limits	6.72–65.88°
Data collected	$-13\le h\le 12, -12\le k\le 12, -13\le l\le 13$
No. of data collected	4290
No. of unique data, including $F_o^2<0$	146 (R_{int}=0.059)
No. of unique data, with $F_o^2>2\sigma(F_o^2)$	128
No. of variables	10
$R(F)$ for $F_o^2>2\sigma(F_o^2)$ [a]	0.022
$R_w(F_o^2)$ [b]	0.064
Goodness of fit	1.23
$(\Delta\rho)_{max}$, $(\Delta\rho)_{min}$ (e Å^{-3})	2.49, −2.51
Positional and displacement parameters [c]	
Dy at 8c (¼, ¼, ¼)	
U_{eq} (Å^2)	0.0095(3)
Cr at 2a (0, 0, 0)	
U_{eq} (Å^2)	0.0131(9)
Ga1 at 12e (x, 0, 0)	
x	0.2895(2)
U_{eq} (Å^2)	0.0119(3)
Ga2 at 12d (¼, 0, ½)	
U_{eq} (Å^2)	0.0105(3)
Interatomic distances (Å)	
Dy–Ga2 (×6)	3.0307(5)
Dy–Ga1 (×6)	3.0495(5)
Cr–Ga1 (×6)	2.482(2)
Ga1–Ga2 (×4)	2.802(1)
Ga2–Ga2 (×4)	3.031(1)

[a] $R(F)=\sum||F_o|-|F_c||/\sum|F_o|$.

[b] $R_w\left(F_o^2\right)=\left[\sum\left[w\left(F_o^2-F_c^2\right)^2\right]/\sum wF_o^4\right]^{1/2}$; $w^{-1}=\left[\sigma^2\left(F_o^2\right)+(Ap)^2+Bp\right]$ where $p=\left[\max\left(F_o^2,0\right)+2F_c^2\right]/3$.

[c] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.