Combined effect of chemical pressure and valence electron concentration through the electron-deficient Li substitution on the RE_4LiGe_4 ($RE=$La, Ce, Pr, and Sm) system

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ABSTRACT

Four members of the RE_4LiGe_4 ($RE=$La, Ce, Pr, and Sm) system have been prepared by high-temperature reaction method and characterized by X-ray diffractions. All compounds crystallize in the orthorhombic Gd_5Si_4-type structure (space group $Pnma$, Pearson code $oP16$) with bonding interactions for interslab Ge_2 dimers. The Li substitution for rare-earth elements in the RE_4LiGe_4 system leads to a combined effect of the increased chemical pressure and the decreased valance electron concentration (VEC), which eventually results in the structure transformation from the Sm_5Ge_4-type with all broken interslab Ge–Ge bond for the parental RE_5Ge_4 to the Gd_5Si_4-type structure for the ternary RE_4LiGe_4 ($RE=$La, Ce, Pr, and Sm) system. Site-preference between rare-earth metals and Li is proven to generate energetically the most favorable atomic arrangements according to coloring-problem, and the rationale is provided using both the size-factor and the electronic-factor related, respectively, to site-volume and electronegativity as well as QVAL values. Tight-binding, linear-muffin-tin-orbital (TB-LMTO) calculations are performed to investigate electronic densities of states (DOS) and crystal orbital Hamilton population (COHP) curves. The influence of reduced VEC for chemical bonding including the formation of interslab Ge_2 dimers is also discussed. The magnetic property measurements prove that the non-magnetic Li substitution leads to the ferromagnetic (FM)-like ground state for Ce_4LiGe_4 and the co-existence of antiferromagntic (AFM) and FM ground states for Sm_4LiGe_4.

1. Introduction

The family of RE_5Tt_4 ($RE=$rare-earth metals, $Tt=$tetrels) compounds [1] have attracted much attentions from worldwide researchers during the last decade given their interesting and applicable characteristics, such as giant magnetoresistence and colossal magnetostriction [2–4]. In particular, one of its members, $Gd_5Si_2Ge_2$, revealed the giant magnetocaloric effect (MCE) [5] around room temperature in 1997, and this compound was nominated as a potential candidate material for the magnetic refrigeration under ambient condition to replace the conventional vapor-cycle system. Since then, there have been numerous research activities for these types of compounds not only to maximize their giant MCE performance [6,7], but also, more in general, to understand the inter-correlation among composition–structure-property of the RE_5Tt_4 family [5,6b,7c,8]. Among these activities, various substitution

chemistry have been studied through either the cation or anion substitutions using electron richer or poorer elements. Some of the recently reported such compounds include $Gd_{5-x}Y_xTt_4$ ($Tt=$Si, Ge; $0 \leq x \leq 4$) [9], $Gd_{5-x}RE_xGe_4$ ($RE=$La, Lu; $0.05 \leq x \leq 0.4$ for La, $x=0.125$, 0.25 for Lu) [10], $Gd_{5-x}Eu_xGe_4$ ($0 \leq x \leq 2$) [7a,11], $Gd_{5-x}M_xTt_4$ ($M=$Zr, Hf; $Tt=$Si, Ge; $0.5 \leq x \leq 5$) [12], $La_{5-x}Y_xSi_4$ ($0 \leq x \leq 5$) [13], $Zr_{5-x}Hf_xGe_4$ ($0 \leq x \leq 5$) [14], $RE_{5-x}Ca_xGe_4$ ($RE=$La, Ce; $3 \leq x \leq 3.8$) [15], Yb_4MgGe_4 [16], and $RE_{5-x}Mg_xGe_4$ ($RE=$Gd–Tm, Lu, Y; $1.0 \leq x \leq 2.3$) [17] for cation substitution, and $Gd_5Si_{1.5}Ge_{2.5}$ [18], $Gd_5Si_xGe_{4-x}$ ($0 \leq x \leq 3$) [19], $Gd_5Ga_xGe_{4-x}$ ($0 \leq x \leq 2.2$) [20] and $Gd_5Sn_xSi_{4-x}$ ($0 \leq x \leq 3$) [21] for anion substitutions. These comprehensive studies displayed three different, but closely related major crystal structures for this family of compounds with respect to the formation of interslab Ge–Ge dimers: (1) the orthorhombic Gd_5Si_4-type [22] including all interslab Ge_2 dimer bond, (2) the monoclinic $Gd_5Si_2Ge_2$-type [5] having only a half of alternating interslab Ge_2 dimer bond, and (3) the orthorhombic Sm_5Ge_4-type [23] showing all interslab Ge_2 dimer non-bond. However, in spite of numerous substitution studies, investigations for the mixing of monovalent alkali metals with rare-earth metals have been explored to a much less extents as comparing to those using electron richer/poorer cationic elements or even using anionic elements.

In particular, the smallest member of Group 1, Li, particularly caught our attention given that several intriguing effects were expected via the Li substitution, such as (1) the chemical pressure [13] triggered by a significant size difference between host (rare-earth metals) and guest (Li) elements, (2) the structure transformation including the formation of interslab Ge_2 dimer bond as a result of the reduced valence electron concentration (VEC) as well as the chemical pressure [13], and (3) the modified magnetism affected by the non-magnetic element as well as the structure transformation. Previously, there were several reports for the RE_4LiGe_4 system. Pavlyuk et al. firstly reported crystal structures of five members in the system with RE=Y, Gd, Er, Tm, and Lu in 1990 [24], then Xie et al. and Peter et al. added Yb_4LiGe_4 [25,26] on the list with simple electronic calculations and properties. Most recently, Fonasini et al. [27] and Suen et al. [28] also studied some members of the RE_4LiGe_4 system, but all investigations did not go beyond the structural discussion.

In this work, we report more comprehensive systematic investigations for the monovalent Li substituted $RE_4Li_xGe_4$ (RE=La, Ce, Pr and Sm) system. These include studies for the structure transformation caused by both the chemical pressure and the reduced VEC, the site-preference between cationic components based in the coloring-problem [29] and q-value (QVAL) [9], and the magnetic properties influenced by the non-magnetic Li element. Electronic structure calculations were conducted using TB-LMTO method [30] for various structure models, and property measurements included temperature dependent magnetic susceptibility and field dependent magnetization for two members of title phases.

2. Experimental

2.1. Synthesis

All the reaction procedures were conducted under an Ar filled glove-box or vacuum condition. Four title compounds were synthesized using pure elements as purchased from vendors (purity≥99.9%; La – ingot, Alfa; Ce – ingot, Alfa; Pr – ingot, Aldrich; Sm – pieces, Alfa; Li – wire, Alfa; Ge – pieces, Alfa) with the corresponding stoichiometric molar ratios. Each reactant was cut into small pieces and loaded in a Nb-ampoule inside a glove-box, and both ends were sealed by arc-welding under the Ar atmosphere. Rare-earth metals and Li were cleaned by scrapping-off the surface of elements using a scalpel just before loading in a Nb-ampoule. Then the Nb-ampoule was sealed in a secondary container of a fused-silica jacket under vacuum to protect the Nb-ampoule from oxidation during the reaction at the elevated temperature. In particular, the fused-silica jacket including Nb-ampoule was made long enough, so that one of ends protruded outside a tube-furnace. The loaded reactants were initially heated up to 1075 °C by 100 °C/h, hold at the maximum temperature for 5 h, then cooled down to 750 °C by 5 °C/h and annealed there for 2 days. While the samples were stayed at the maximum reaction temperature, the protruded end of the fused-silica jacket outside the furnace was rotated regularly to homogenize reactants mixtures. After the annealing process, the reactants were taken out of the furnace at 750 °C and instantly quenched in the air. Single-phase products of targeted compounds were obtained from Ce and Sm containing compounds showing well-grown crystals with needle/bar-shape morphology and metallic luster. La and Pr analogs produced title phases as a major product as well, but small amounts of La_5Ge_3 or Pr_5Ge_3, respectively, were also included as a secondary phase according to both powder and single crystal X-ray diffraction data. Alternative reaction methods using different temperature profiles or even ice-quenching were unsuccessful to produce single-phase products of La and Pr analogs. All four compounds remained visibly moisture- and air-stable for at least one month.

2.2. Crystal structure determination

The crystal structures of four title compounds were characterized by both powder and single crystal X-ray diffractions at room temperature. Powder X-ray diffraction data of each sample was collected using the step size of 0.05° with the exposure time of 1 h on Bruker D8 diffractometer (monochromatic Cu$K\alpha_1$ radiation, λ=1.54059 Å). The phase purity of each sample was initially checked using the collected powder patterns, and then peaks were indexed to identify phases included in products using program Rietica [31]. Overall lattice parameters of title compounds linearly decreased as the size of rare-earth metals decreased from La to Sm, and the resultant peak shifting toward higher angles was observed on powder X-ray diffraction patterns.

Single crystal X-ray diffraction data were collected at room temperature using Bruker SMART APEX2 CCD-based diffractometer equipped with Mo$K\alpha_1$ radiation (λ=0.71073 Å). Firstly, several silvery lustrous needle/bar-shape crystals were selected from each batch of products, and their qualities were briefly checked by a rapid scan. After that, the best crystals were chosen for the further data collection. Full data collection was processed by the Bruker's APEX2 software [32]. Data reduction, integration and unit cell refinements were conducted using SAINT program [33], and semi-empirical absorption correction based on equivalents was performed using SADABS [34]. The program XPREP in SHELXTL software package was exploited to sort and merge the structure factors [35]. The crystal structure was solved by direct methods and refined to convergence by full matrix least-squares methods on F^2. Refined parameters include the scale factor, the atomic positions with anisotropic displacement parameters (excluding Li), and extinction coefficients. During the last refinement cycle, atomic positions were standardized using STRUCTURE TIDY [36].

A recent article for the $RE_{5−x}Li_xGe_4$ (RE=Nd, Sm and Gd) series reported by Suen et al. claimed that the small homogeneity width was observed in their compounds with $x\approx$1.03 [28]. Authors mentioned that two particular observations supported their arguments, which were the peaks shifting in powder X-ray diffraction data as Li contents varied, and the underoccupancy of the $RE2$ site in all three compounds. During our structure refinement, we attempted to refine the $RE2$ site as being freed from the occupancy factor, but the site was refined with 100% occupancy of La and Ce, respectively, in La_4LiGe_4 and Ce_4LiGe_4. Therefore, we did not pursue any further refinement using a mixed-occupancy at the $RE2$ sites for these two compounds. However, we observed ca. 0.16% and 0.9% of underoccupancy at the $RE2$ sites, respectively, in the Pr and Sm compounds. Thus, these sites were refined as mixed-sites of rare-earth metals and Li, and the final compositions turned out to be $Pr_{3.997(3)}Li_{1.003}Ge_4$ and $Sm_{3.982(3)}Li_{1.018}Ge_4$. However, for the Pr compound, it was hard to say that there existed a mixing of Pr and Li at the $RE2$ site since the amount of mixing was within a deviation, and even the R-values were identical with and without the mixing. Thus, we eventually exploited a fixed occupation for Pr at the $RE2$ site resulting in a stoichiometric composition of Pr_4LiGe_4. On the other hand, for the Sm analog, the amount of disorder was still very slight, but not neglectful. Moreover, in addition to the refined composition and the lattice parameters, which were very close to the previous report from Suen et al. [28], the Hamilton test [37] for the statistical significance of the mixed-occupancy also proved that the refinement with the disorder was a better result. Therefore, we eventually confirmed a small phase width for $Sm_{4−x}Li_xGe_4$ ($x\approx$1.018(3), Sm_4LiGe_4 hereafter). Although the crystallographic data of $Sm_{4−x}Li_xGe_4$ was recently reported by Suen et al. we used our data here for consistency since all our data were collected at room temperature, whereas Suen's was collected at 200 K. Interestingly, the recently reported Er analog [38] showed even the higher Li content at the $RE2$ site than the Sm compound. Important crystallographic data, atomic positions, atomic displacement parameters and selected interatomic distances of four title compounds are listed in