Complex Crystal Chemistry of $\text{Yb}_6(\text{CuGa})_{50}$ and $\text{Yb}_6(\text{CuGa})_{51}$ Grown at Different Synthetic Conditions

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Abstract

Two new compounds in the Yb–Cu–Ga system have been discovered. $\text{Yb}_6(\text{CuGa})_{50}$ has been obtained as single crystals grown from gallium metal flux and $\text{Yb}_6(\text{CuGa})_{51}$ has been synthesized by high-frequency heating technique. Structure analysis reveals new structure type for $\text{Yb}_6(\text{CuGa})_{50}$ ($C2/m$ space group) while $\text{Yb}_6(\text{CuGa})_{51}$ crystallizes in rhombohedral space group $R\bar{3}m$ adopting the $\text{Th}_2\text{Zn}_{17}$ structure type. Both structures could be derived from the simplest layered packing, through CaCu_5 -type structure, as a common parent. Physical properties of the sample obtained in bulk quantity $\text{Yb}_6(\text{CuGa})_{51}$ have been explored. The magnetic susceptibility study of $\text{Yb}_6(\text{CuGa})_{51}$ in the temperature range 2–300 K, suggests a valence fluctuation at lower temperatures. XANES study suggests that Yb exists in mixed valent state in $\text{Yb}_6(\text{CuGa})_{51}$. Electrical resistivity measurement reveals that $\text{Yb}_6(\text{CuGa})_{51}$ is metallic in nature and shows Fermi-liquid behavior in the temperature range of 3.5 to 25 K.

Keywords: Crystal growth; Intermetallics; XANES; Magnetism; Resistivity.

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1. Introduction

Exploration of new material using metal flux single crystal growth technique always has drawn the attention of solid-state chemists. The high temperatures involved during this synthesis technique restrict the synthesis of compounds in various ways. Since the heating and annealing step is very slow, these reactions often lead to the most thermodynamically stable products. There is very rare chance to get kinetic control over the products as the high energies involved during the course of the reaction.¹ The other criterion to explore new materials is the selection of elements, especially those with multiple valences. For example – the presence of an unstable electronic $4f$ electron shell can cause the Yb ion to show two energetically closely spaced electronic configurations $4f^{13}$ and $4f^{14}$ with magnetic Yb^{3+} and nonmagnetic Yb^{2+} states, respectively. Generally, the hybridization (interaction) strength among the magnetic $4f$ electrons and the s , p , and d conduction electrons determines the stability of the different ground states.²⁻⁵ Because of the existence of its two energetically similar electronic configurations, Yb based compounds show intermediate valency, strong electron correlation, heavy fermion superconductivity, Kondo lattice behavior, antiferromagnetic behavior.⁶⁻¹⁰ Structurally, Yb-containing ternary intermetallic systems contain diverse compounds, which often crystallize in the own, unique, structure types. There have been discoveries of new Yb based interesting compounds in recent past - YbCuGa_3 ,¹¹ Yb_4TGe_8 ,¹² $\text{YbMn}_{0.33}\text{Si}_{3.67}$,¹³ $\text{Yb}_3\text{AuGe}_2\text{In}_3$,¹⁴ $\text{YbGe}_{2.83}$,¹⁵ YbGa_4Ge_2 ,¹⁶ $\text{Yb}_3\text{Ga}_4\text{Ge}_6$.¹⁷ This background motivated us to find more new compounds with a particular focus on Yb-Cu-Ga systems as not many compounds reported in this family. The known examples are YbCu_4Ga ,¹⁸ YbCu_3Ga_2 ,¹⁹ $\text{Yb}_3\text{Cu}_{4.4}\text{Ga}_{6.6}$,²⁰ $\text{YbCu}_{0.8}\text{Ga}_{1.2}$,²¹ YbCuGa_3 ¹¹ and $\text{YbCu}_{0.15}\text{Ga}_{3.85}$.²²

One of the most common structure type for ternary compounds with rare-earth (RE) and transition metal (T) /metalloid (X) is $\text{Th}_2\text{Zn}_{17}$ with T/X statistical mixing. There are a very few ternary compounds reported with $RE_2(\text{CuGa})_{17}$ composition (*e.g.*, $\text{Dy}_2\text{Cu}_{8.45}\text{Ga}_{8.55}$,²⁰ $\text{Er}_2\text{Cu}_{11.5}\text{Ga}_{5.5}$,²³ $\text{Ho}_2\text{Cu}_{8.9}\text{Ga}_{8.1}$,²⁴ $\text{Lu}_2\text{Cu}_{12.25}\text{Ga}_{4.75}$,²⁵ $\text{Sm}_2\text{Cu}_{11.4}\text{Ga}_{5.6}$ ²⁶). It is a well-established fact that the compounds crystallizing in $\text{Th}_2\text{Zn}_{17}$ crystal structure type show tremendous physical properties. For examples, $\text{Sm}_2\text{Co}_{17}$ ²⁷ magnet shows uniaxial anisotropy while Y_2Co_{17} and $\text{Pr}_2\text{Co}_{17}$ exhibit planar anisotropy. $RE_2\text{Fe}_{17}$ ($RE = \text{La}, \text{Ce}, \text{Sm}, \text{Gd}, \text{Tb}, \text{Y}$) compounds have high

saturation magnetization and are generally collinear ferromagnets with Curie temperature (T_c) in the range of 300 K. Pearson's Crystal Data (PCD)²⁸ and Inorganic Crystal Structure Database (ICSD)²⁹ reveals more than 860 compounds are reported in the $\text{Th}_2\text{Zn}_{17}$ structure prototype. Among them, several *RE* based pseudo-ternary compounds having $\text{Th}_2\text{Zn}_{17}$ structure type are well studied with various physical properties. $\text{RE}_2\text{Fe}_{17-y}\text{M}_y$ ($\text{M} = \text{Al, Ga, Si}$) compounds show remarkable variation in their structural aspect, magnetic ordering and Curie temperature (T_c) upon different substitution of X at Fe position(s).³⁰⁻³⁵ For example, $\text{Sm}_2\text{Fe}_{17-y}\text{M}_y$ compounds ($\text{M} = \text{Al, Ga, Si}$) with y up to 2 show an appreciable enhancement in the Curie temperature T_c .³⁶⁻³⁸ $\text{RE}_2\text{Mn}_{17-y}\text{M}_y$ ($\text{M} = \text{Al, Ga, Si}$) compounds also reveal Curie Weiss behavior and low-temperature antiferromagnetic ordering.³⁹ $\text{Ce}_2\text{Fe}_{17-x}\text{Si}_x$ is another example where substitution of Si for Fe increase T_c from 238 K to 455 K.³¹ Helicoidal magnet $\text{Ce}_2\text{Fe}_{17}$ transforms to a collinear ferromagnet when Fe is partially doped by Al or Si.³¹ Due to mentioned properties like high saturation magnetization and collinear magnetism these compounds have applications as high energy product magnets.

In current work, we have explored two new compounds in the Yb–Cu–Ga system - $\text{Yb}_6(\text{CuGa})_{50}$ and $\text{Yb}_6(\text{CuGa})_{51}$. Interestingly, the change of synthesis strategy causes a dramatic change in the structural variation with the addition/removal of a Cu/Ga atom. Among them $\text{Yb}_6(\text{CuGa})_{50}$ is a new structure type. We have discussed the relation between the crystal structure of the compounds in detail. The chemical and physical properties of $\text{Yb}_6(\text{CuGa})_{51}$ have been studied as it was obtained in a large quantity from high-frequency induction heating (HFIH).

2. Experimental Section

2.1. Reagents: The as purchased reagents were used for the synthesis without any additional purification: Ytterbium (in the form of pieces cut from the metal chunk, 99.99%, Alfa Aesar), copper (shots, Sigma Aldrich, 99.99%) and gallium (pieces, Alfa Aesar, 99.999%).

2.2. Synthesis

2.2.1. $\text{Yb}_6(\text{CuGa})_{50}$: Metal Flux method

Single Crystals were grown through metal flux growth technique using excess gallium flux by combining Yb metal, Ga pieces, and Cu shots in a niobium ampoule. The ampoule was

kept inside a fused silica tube (13-mm), followed by flame-sealing under a vacuum of 10^{-6} Torr to avoid any chance of oxidation while heating. The temperature of the reactants was raised to 1273 K over 10 hr and kept at this temperature for 2 h to homogenize the melt adequately. Next, the melt temperature was cooled down to 1073 K within 2 h and maintained at this temperature for 48 h. The silica tube containing the ampoule was then allowed to cool gradually to 300 K over 48 h. No reactions between the niobium ampoule and starting materials or product were detected. To separate the reaction product from the melt containing excess gallium flux, the reaction content was reheated to 673 K and subsequently centrifuged immediately. To clean the surface containing residual Ga, crystals were immersed in 2–4 M I_2 in dimethylformamide over 6 h followed by sonication at room temperature. The crystals were then dried with acetone. The gray color rod shaped single crystals of $Yb_6(CuGa)_{50}$ were obtained in high yield (>90%). Several crystals, which were grown as shining as metallic silver plates, were carefully hand-picked for further analysis.

2.2.2 $Yb_6(CuGa)_{51}$: High-frequency induction heating

Yb, Cu, and Ga were taken in 2:11:6 atomic ratio. The precursors were sealed inside a tantalum ampoule under Ar atmosphere using Edmund Buhler GmbH MAM-1 arc melter. The ampoule was then kept in a water-cooled sample chamber in the Easy Heat induction heating system, Model 7590. The reaction was carried out at 180 Amperes (approximately 1200 – 1300 K) for 50 min followed by rapid cooling to room temperature by reducing the current to zero Ampere. The light gray shining and highly crystalline product $Yb_6(CuGa)_{51}$ was obtained. No side products and reactions with the ampoule could be detected. No more than 1% weight loss was observed in the product. The stability of the compound $Yb_6(CuGa)_{51}$ was checked by taking XRD at the interval of two weeks for a period of three months and was found to be stable under ambient conditions. The obtained sample was used for further magnetic and resistivity measurements.

2.3. Powder X-ray Diffraction

Phase identity and purity of the bulk $Yb_6(CuGa)_{51}$ sample synthesized using HFIH was determined by X-ray powder diffraction using Bruker D8 Discover diffractometer (Cu- $K\alpha$ radiation; $\lambda = 1.5406 \text{ \AA}$). The experimental XRD powder pattern of $Yb_6(CuGa)_{51}$ contains

preferential orientation in particular [113] direction and also observed in higher order reflection (**Figure 1**) however, the zoomed X-ray diffraction pattern (**Figure S1**) compared with the simulated pattern from the single-crystal XRD structure refinement of the rhombohedral structure confirms the phase purity (**Figure 1**).

2.3. Elemental Analysis

The single crystals obtained from the reactions using flux growth technique and HFIH technique were used for semi-quantitative microanalyses using a Leica 220i scanning electron microscope equipped with Bruker 129 eV energy dispersive X-ray spectroscopy detector. The accelerating voltage of 20 kV for 90 s accumulation time was applied for data acquisition. SEM image of a typical single crystal of flux-grown $\text{Yb}_6(\text{CuGa})_{50}$ and HFIH-grown $\text{Yb}_6(\text{CuGa})_{51}$ are shown in **Figure 2a** and **2b** respectively. On visibly clean surfaces of the single crystals, the EDS analyses were performed which indicated that flux-grown crystal covered in residual Ga showed element ratio different from expected (**Figure S2**), while the atomic composition of $\text{Yb}_6(\text{CuGa})_{51}$ was in a good agreement with loaded stoichiometry (**Figure S3**).

2.4. Single-Crystal X-ray Diffraction

X-ray diffraction data were collected on selected single crystals of $\text{Yb}_6(\text{CuGa})_{50}$ and $\text{Yb}_6(\text{CuGa})_{51}$ using a Bruker Smart Apex II CCD diffractometer equipped with a typical focus, 2.4 kW sealed tube X-ray source, operating at 50 kV and 30 mA with graphite monochromatic Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) with ω scan mode. With the help of commercially available super glue, the rod-shaped metal flux grown single crystals and plate-like crystals obtained from HFIH were mounted on a thin glass fiber ($\sim 0.1 \text{ mm}$) (**Figure S4**). A half-sphere (data were collected in the monoclinic system) of 60 frames was acquired up to 68.78° in 2θ . The individual frames were measured at an exposure time of 10 s per frame with steps of 0.5° . While in the case of $\text{Yb}_6(\text{CuGa})_{51}$, matrix collection suggested a rhombohedral crystal system, however, because of ambiguity in the phase and composition of this compound the complete data were collected same as the previous crystal (*i.e.*, monoclinic crystal system up to 60.542° in 2θ). The integration of diffraction profiles was performed using program SAINT,⁴⁰ and SADABS⁴¹ program was used to perform the absorption correction. Based on the systematic absences, the space group were determined - $C2/m$ for $\text{Yb}_6(\text{CuGa})_{50}$ and $R\bar{3}m$ for $\text{Yb}_6(\text{CuGa})_{51}$. With WinGx system, ver.

1.80.05⁴² the Platon program was used to check the additional symmetry. SHELXS 97 was used to solve structure and was refined using full matrix least-squares method using SHELXL⁴³ with anisotropic atomic displacement parameters (ADP) for all atoms. Diamond⁴⁴ was used to generate the packing diagrams. To confirm the correct composition, the refinement for occupancy parameters was performed in a distinct series of least-squares cycles.

Suspecting the phase transition driven by an extra Cu or Cu/Ga in Yb₆(CuGa)₅₁ compared to Yb₆(CuGa)₅₀, we have performed single crystal X-ray diffraction in the temperature range of 100–400 K for Yb₆(CuGa)₅₁. The temperature dependent single crystal XRD studies were carried out using Bruker Photon 100 CMOS detector in shutter less mode equipped with a micro focus, 5 kW sealed tube X-ray source operating at 50 kV and 30 mA, with ω scan mode with graphite monochromatic Mo-K α radiation ($\lambda = 0.71073$ Å).

2.5. Structure refinement

Metal flux grown Yb₆(CuGa)₅₀ was refined in *C2/m* space group with lattice constants $a = 21.1312(16)$ Å, $b = 3.8279(3)$ Å, $c = 9.5698(7)$ Å, $\alpha = 90^\circ$, $\beta = 99.467(4)^\circ$, $\gamma = 90^\circ$. The final refinement resulted in a shorter bond length among Yb-Yb, Yb-Cu, and Yb-Ga pairs. The shortest bond length of $3.8279(4)$ Å compared to 3.88 Å indicates the mixed valence of Yb suggesting the ionic nature of the compound.^{2,14} While in the case of HFIH synthesized single crystal Yb₆(CuGa)₅₁, first, data was tried to be solved and refined in monoclinic space group *C2/m*. The first least square refinement gave the negative displacement parameters for all assigned atoms including the heaviest element in the system – Yb. This indicated the wrong assignment of space group during XPREP, which was further confirmed by high weighted refinement values and residual electron densities. So, the space group selection using XPREP was again performed but in suggested rhombohedral crystal system; SG: $R\bar{3}m$. Now, the first cycle of least square refinement gave all parameters in acceptable range except the Yb-Cu and Yb-(Cu/Ga) bond distances because of the presence of Yb as Yb³⁺, confirmed from XANES study. The final refinement suggests Yb₆(CuGa)₅₁ crystallizes in the Th₂Zn₁₇ structure type with lattice constants $a = b = 8.6964(2)$ Å and $c = 12.7062(5)$ Å.

The details of data collection and room temperature structure refinement are listed in **Table 1**, and the details about data collected at 100 K, 200 K, and 400 K for Yb₆(CuGa)₅₁ crystal

is listed in **Table S1**. **Table S2 and S3** list the standard atomic positions, and isotopic atomic displacement parameters of these compounds are given in. **Table S4 and S5** contain the anisotropic displacement parameters and important bond lengths.

2.6. Magnetic Measurements

Magnetic measurement on finely powdered $\text{Yb}_6(\text{CuGa})_{51}$ was carried out using Quantum Design MPMS-SQUID magnetometer. Applying a magnetic field of 1000 Oe, temperature dependent data were collected between 2 and 300 K in the field cooled mode. Also, sweeping from -60 kOe to 60 kOe magnetization data were also collected for $\text{Yb}_6(\text{CuGa})_{51}$ at 2 K and 300 K.

2.7. Electrical Resistivity

The pressed pellet made of single crystals of $\text{Yb}_6(\text{CuGa})_{51}$ was used to perform the resistivity measurement in the temperature range 3-300 K without any applied magnetic field with a conventional AC four probe set-up using Quantum Design Physical Property Measurement System (QD-PPMS). Actively conducting silver epoxy paste was used to give contact with four thin copper wires to the pellet.

2.8 X-ray absorption near edge spectroscopy (XANES)

XANES experiment on $\text{Yb}_6(\text{CuGa})_{51}$ was performed at DESY, Germany using the P65 beamline PETRA III. The measurement was carried out in transmission mode at the Yb L_{III} -edge at ambient pressure using gas ionization chambers in order to monitor the incident and transmitted X-ray intensities. Si [111] double crystal monochromator generated the monochromatic X-rays, calibrated by defining the inflection point (first derivative maxima) of Cu foil as 8980.5 eV. To record the incident (I_0) and transmitted (I_t) photon intensities at different edges simultaneously, ionization chambers filled with appropriate gases were used. PIPS detector was used for the fluorescent signals. Mixing the sample with an inert cellulose matrix homogeneously, pellets for the measurements were prepared to have an X-ray absorption edge jump close to one.

3. Results and Discussion

The initial attempt of the synthesis was to discover new compounds within the Yb-Cu-Ga family using Ga as the active flux. The reaction run in liquid gallium resulted in $\text{Yb}_6(\text{CuGa})_{50}$

which was confirmed by single crystal XRD. Since Cu and Ga have only 2 electrons difference, it is not easy to identify the exact position of both using XRD. So, our refinement resulted in three positions with both Cu and Ga atoms.

In order to achieve the metal flux grown phase, i.e., $\text{Yb}_6(\text{CuGa})_{50}$ in bulk quantity, several reactions were run by varying the reaction parameters such as the current employed and time for the total reaction using HFIH. First, the reaction current was varied from 180 amp to 170 amp and 190 amp in order to decrease and increase the melt temperature while maintaining the same reaction time and same starting elemental ratio. However, we noticed that the powder XRD mismatched with the simulated XRD pattern obtained from the single crystal XRD structure refinement of $\text{Yb}_6(\text{CuGa})_{50}$ (metal flux product). Instead, it resulted in $\text{Yb}_6(\text{CuGa})_{51}$ phase, which was characterized by single crystal XRD, powder XRD and EDX measurement (since an excess of Ga flux was not an issue in this case). Almost same result was found when the reaction time was varied for 10 minutes.

Assuming the fact that the structural change could be happening due to the insertion of additional one Cu or Ga or Cu/Ga in $\text{Yb}_6(\text{CuGa})_{50}$ structure which may lead a phase transition to $\text{Yb}_6(\text{CuGa})_{51}$, the starting elemental composition were also varied i.e. $\text{Yb}_6\text{Cu}_{50}$, $\text{Yb}_6\text{Cu}_{40}\text{Ga}_{10}$, $\text{Yb}_6\text{Cu}_{30}\text{Ga}_{20}$, $\text{Yb}_6\text{Cu}_{20}\text{Ga}_{30}$, $\text{Yb}_6\text{Cu}_{10}\text{Ga}_{40}$ and $\text{Yb}_6\text{Ga}_{50}$. Although these variations resulted in a decent amount of crystals with good quality, they could not be refined using single crystal XRD. The powder XRD revealed that the compounds formed were having the unknown mixed phases (**Figure S5**).

3.1 Crystal chemistry

The crystal structure of $\text{Yb}_6(\text{CuGa})_{50}$ and $\text{Yb}_6(\text{CuGa})_{51}$ along *b*-axis and *c*-axis, respectively are shown in **Figure 3** along *c*-axis. $\text{Yb}_6(\text{CuGa})_{50}$ crystallizes in a new structure type with $C2/m$ space group with thirteen atomic positions. $\text{Yb}_6(\text{CuGa})_{51}$ crystallizes in the $\text{Th}_2\text{Zn}_{17}$ crystal structure type (SG: $R\bar{3}m$) with five atomic positions.^{23,25} The coordination environments of Yb atoms in both refined structures are similar (**Figures 4 and 5**). Yb atom has distorted six capped hexagonal prism coordination environments, which is a typical environment around a large atom, known as a cage (**Figure 5 and S6**). In $\text{Yb}_6(\text{CuGa})_{51}$ structure, cages share top and bottom hexagons (Cu₃/Ga₃ (M3) sites), forming tunnels along *c* direction (**Figure 4**). Thus, Yb

can be regarded as being split into two M3 positions in the alternate sequence. The alternate M3 has the same coordination environment as Yb has. The two tunnels share the edges formed by the Cu and Ga atoms.

While in the case of refined $C2/m$ crystal structure, the construction of the single tunnel is similar, but it does not share edges with the neighboring tunnel (**Figure 4**). Instead, the neighboring tunnel can be regarded as being rotated by an angle of 30° with a change in alternate surrounding layers to the central atom. In this case, the two tunnels are joined by the M3 atoms, which has different coordination environment as four capped tetragonal prism compared to 12 hexagonal antiprism coordination environment in $R\bar{3}m$ structure.

To study possible phase transition, temperature-dependent single crystal data was also collected at 100, 200, 298 and 400 K for $\text{Yb}_6(\text{CuGa})_{51}$. The lattice parameters increase as temperature increases due to increased thermal lattice vibrations. Consequently, the unit cell volume increases. Since there is only two electrons difference between Cu and Ga atoms, the scattering factor of both are almost similar, and so, it is difficult to differentiate between them which sometimes leads discrepancy in the assignment of Cu and Ga positions. Successful refinement of all the temperature dependent data in similar lattice parameters with rhombohedral space group $R\bar{3}m$ discarded any phase transition possibility.

To understand the relation between these two crystal structures having different space groups we have performed a detailed structural relation by visualization (**Figure 6**) and analyzing the Wyckoff sites and co-ordination environment of atoms within the unit cell (**Figure 4, 5 and 6**).

Both compounds in Yb–Cu–Ga systems are examples of layered structures with a typical for RE atom environment – six-capped hexagonal prism (CN = 18), optionally with additionally capped hexagons from top and bottom with CN = 20. To visualize $\text{Yb}_6(\text{CuGa})_{51}$ structure, we propose a derivation from a single square array of atoms, or in other words single-atom primitive cubic cell, known as α -Po-type structure (**Figure 6 and 7**). Distortion of the α -Po-type structure into a perfect hexagonal cell results into the $\text{Hg}_{0.1}\text{Sn}_{0.9}$ -type structure in $P6/mmm$ space group. Further transformation and ordering of atomic sites lead to CaCu_5 structure type, a typical structure for systems with the large electropositive element and a transition metal. The CaCu_5 -

type structure can be described as close-packed honeycomb tunnels with an infinite line of large atoms arranged in c direction. Introduction of another smaller size metal in the structure leads to partial substitution of the large electropositive metal site to a split site dumbbells, with an environment of hexagonal antiprism around each end of the dumbbell ($2 \times$ hexagonal antiprism = six-capped hexagonal prism). This site split phenomenon is also observed in other systems of metallic systems and metalloids, where position splitting may result in an increased number of layers or might be observed as a static disorder.^{45,46} Interestingly, the large electropositive metal site and dumbbells, as a result of splitting of this site, may be found in different proportions with alternating sequence ($RE - M_2$) as it occurs in $\text{Th}_2\text{Ni}_{17}$ -type structure (listed in the **Table S2**), or in more complex ratios ($RE - RE - M_2$) as it is observed in $\text{Th}_2\text{Zn}_{17}$ -type structure. Minor distortion from ideal hexagons results in $\text{Yb}_6(\text{CuGa})_{51}$ structure, which adopts $\text{Th}_2\text{Zn}_{17}$ -type structure.

At first sight, the other compound $\text{Yb}_6(\text{CuGa})_{50}$ obtained by metal flux technique is compositionally close to $\text{Yb}_6(\text{CuGa})_{51}$ structure but has a significant difference in the structural pattern (**Figure 6** and **8**). However, both structures are related through CaCu_5 -type six-capped hexagonal prism environment of Yb atom and share common structural features through α -Po-type fragments. Primitive α -Po-type cubic cell transforms into another primitive cubic cell, with an additional atom at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ position – CsCl-type structure. The CsCl-type structure provides its distorted fragments to alternate CaCu_5 -type fragments in the structure $\text{Yb}_6(\text{CuGa})_{50}$ ($C2/m$ space group). This way of describing similar complex structure patterns is borrowed from the work done by Kanatzidis and co-workers, which shows CaCu_5 -type fragments occurring with NaCl-type fragments, as it is reported for $\text{Cs}_{1-x}\text{Sn}_{1-x}\text{Bi}_{9+x}\text{Se}_{15}$ series of compounds.⁴⁷

4 Physical Properties

4.1 Magnetism

Magnetic studies were performed on a finely powdered sample obtained from highly crystalline compound $\text{Yb}_6(\text{CuGa})_{51}$ synthesized by HFIH technique. The molar magnetic susceptibility (χ_m) of $\text{Yb}_6(\text{CuGa})_{51}$ (**Figure 9**) and inverse susceptibility ($1/\chi_m$) at an applied field of 1000 Oe (**Figure 9**) suggest the weak paramagnetic behavior of the compound at room temperature with an antiferromagnetic ordering at 2.5 K. The magnetic moment at room

temperature was found to be an ambiguous value of $3.05 \mu_B/\text{Yb atom}$ by using the formula $\mu_{\text{eff}} = 2.83 \sqrt{T \chi_m}$, (where T is the temperature in kelvin and χ_m is magnetic susceptibility in emu.mol^{-1}) which suggests Yb exists in its mixed valent state. To further investigate the oxidation state of Yb and quantify it in the compound, XANES study was performed at room temperature (**Figure 10**), which confirmed that Yb exists in the mixed valent state with ~60% of Yb^{3+} . With the decrease in temperature, valence fluctuation was observed which is very common in multivalent rare earth based materials such as Ce, Sm, Eu and Yb based materials.⁴⁸⁻⁵² At lower temperatures, the magnetic susceptibility of $\text{Yb}_6(\text{CuGa})_{51}$ slightly increases with increasing field which is very common for *RE* based intermetallics.^{14,53} Magnetic impurities and/or crystal field contributions can be accounted for this deviation. The field dependence of the magnetization for ground sample $\text{Yb}_6(\text{CuGa})_{51}$ was measured at 2 K and 300 K, (**Figure S7**) which further confirmed the paramagnetic behavior of the compound.

4.2 Electrical resistivity

The electrical resistivity of $\text{Yb}_6(\text{CuGa})_{51}$ (**Figure 11**) decreases linearly with temperature, which is typical for metallic systems.^{54,55} There was no long-range magnetic ordering observed. The resistivity value of $\text{Yb}_6(\text{CuGa})_{51}$ is $412.76 \mu\Omega\text{cm}$ at room temperature. To investigate the status of conduction electrons' correlative nature in the low-temperature range of 3.5–25 K, the $\rho(T)$ data was fitted with Power law, $\rho = \rho_0 + AT^n$ (ρ_0 = residual resistivity; A and n = fitting parameters). Experimentally observed ρ proportional to T^2 suggests the domination of electron-electron scattering over electron-phonon scattering. The non-linear fitting in the mentioned temperature range gives residual resistivity $\rho_0 = 340.06 \Omega\text{cm}$ with $n = 2.3$. in the compound $\text{Yb}_6(\text{CuGa})_{51}$, which is the scenario for systems having Fermi liquid behavior.^{16,56,57} To confirm the Fermi liquid and non-Fermi liquid behavior, the resistivity data was plotted as $(\rho - \rho_0)$ vs. T^2 (as shown in inset; **Figure 11**). The linearity in the data confirms a strongly correlated fermi liquid state at low temperature. The residual resistivity ratio (RRR, $\rho_{300}/\rho_0 = 1.21$) confirms the sample is highly pure..⁵⁸

5. Conclusion

There are very few reports in Yb–Cu–Ga family and most of them crystallize either in tetragonal (SG: $I4/mmm$) or hexagonal (SG: $P6/mmm$) crystal systems except our recent report

on monoclinic YbCuGa₃ (SG: $C2/m$). It is crucial to note that the metal flux technique has been used to discover several new compounds. YbCuGa₃ is an example which we have discovered in the Yb–Cu–Ga family. During the course of our systematic study to discover other new compounds in the Yb–Cu–Ga family, we obtained the single crystals of Yb₆(CuGa)₅₀ from the reactions using gallium as active flux which crystallizes in a new structure type with monoclinic SG: $C2/m$. During our attempt to scale up the synthesis, the HFIH technique led us to discover Yb₆(CuGa)₅₁, a new compound in the family and another ternary variant of the Th₂Zn₁₇ structure prototype in rhombohedral SG: $R\bar{3}m$. The structural relationship between these two compounds has been established in detail. Both structures can be derived from simple layered parents, form typical six-capped hexagonal prism cage around Yb atom, but in Yb₆(CuGa)₅₁ structure, cages align to form a tunnel. The change in the synthesis conditions causes a dramatic change in crystal structure, which we believe can use as one of the tools to generate new compounds with new structure types.

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Supporting Information Available:

X-ray crystallographic file in CIF format; crystallographic tables for crystal data, structure refinement, atomic coordinates and anisotropic displacement parameters; analyses from powder XRD patterns; EDX and magnetization curves. This material is available free of cost via the Internet at <http://pubs.acs.org>.

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Table 1. Crystal data and structure refinement for Yb₆(CuGa)₅₀ and Yb₆(CuGa)₅₁.

	Yb₆(CuGa)₅₀	Yb₆(CuGa)₅₁
Empirical formula	Yb_{0.75}Cu₄Ga_{2.25}	Yb_{0.75}Cu_{3.89}Ga_{2.48}
Formula weight	540.81	550.17
Temperature	293(2) K	296(2) K
Wavelength	0.71073 Å	
Crystal system	Monoclinic	Rhombohedral
Space group	<i>C2/m</i>	<i>R$\bar{3}m$</i>
Unit cell dimensions	<i>a</i> = 21.1312(16) Å, α = 90° <i>b</i> = 3.8279(3) Å, β = 99.467(4)° <i>c</i> = 9.5698(7) Å, γ = 90°	<i>a</i> = 8.6964(2) Å, α = 90° <i>b</i> = 8.6964(2) Å, β = 90° <i>c</i> = 12.7062(5) Å, γ = 120°
Volume	763.54(10) Å ³	832.20(5) Å ³
Z	8	
Density (calculated)	9.409 g/cm ³	8.782 g/cm ³
Absorption coefficient	55.421 mm ⁻¹	51.785 mm ⁻¹
F(000)	1906	1939
Crystal size	0.04 x 0.070 x 0.090 mm ³	0.05 x 0.08 x 0.09 mm ³
θ range for data collection	1.954 to 34.389°	3.144 to 30.271°
Index ranges	-28 ≤ <i>h</i> ≤ 31 -5 ≤ <i>k</i> ≤ 4 -12 ≤ <i>l</i> ≤ 13	-11 ≤ <i>h</i> ≤ 11 -10 ≤ <i>k</i> ≤ 11 -12 ≤ <i>l</i> ≤ 16
Reflections collected	4041	2501
Independent reflections	1388 [<i>R</i> _{int} = 0.0596]	307 [<i>R</i> _{int} = 0.0752]
Completeness to θ = 24.978°	100%	
Refinement method	Full-matrix least-squares on <i>F</i> ²	
Data / restraints / parameters	1388 / 0 / 88	307 / 0 / 26
Goodness-of-fit	1.063	1.143
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> _{obs} = 0.0514, <i>wR</i> _{obs} = 0.1337	<i>R</i> _{obs} = 0.0274, <i>wR</i> _{obs} = 0.0627
<i>R</i> indices [all data]	<i>R</i> _{all} = 0.0633, <i>wR</i> _{all} = 0.1434	<i>R</i> _{all} = 0.0280, <i>wR</i> _{all} = 0.0631
Extinction coefficient	0.00150(18)	0.00144(12)
Largest diff. peak and hole	4.633 and -4.477 e·Å ⁻³	2.807 and -2.938 e·Å ⁻³

$$R = \sum ||F_o| - |F_c|| / \sum |F_o|, wR = \{ \sum [w(|F_o|^2 - |F_c|^2)^2] / \sum [w(|F_o|^4)] \}^{1/2} \text{ and } w = 1 / [\sigma^2(F_o^2) + (0.0546P)^2 + 128.1452P]$$

where $P = (F_o^2 + 2F_c^2) / 3$

Figure 1. Comparison of powder XRD pattern of $\text{Yb}_6(\text{CuGa})_{51}$ with simulated pattern obtained from the single crystal structure refinement.

Figure 2. SEM image of a typical single crystal of (a) flux grown $\text{Yb}_6(\text{CuGa})_{50}$ and (b) high-frequency induction heated $\text{Yb}_6(\text{CuGa})_{51}$.

Figure 3. The crystal structure of (a) $\text{Yb}_6(\text{CuGa})_{50}$ and (b) $\text{Yb}_6(\text{CuGa})_{51}$ are shown along the b and c -axis respectively.

Figure 4. The construction of structural motif from the Yb (blue colored atom) and mixed (Ga3/Cu3 shown by green colored atoms) coordination atmospheres in $\text{Yb}_6(\text{CuGa})_{51}$ compound (S.G. $R\bar{3}m$). To relate this structure with $C2/m$ the colors of Cu and Ga atoms are maintained as in the previous case, however, the violet and orange color atoms, in this case, are actually mixed atoms except for the red colored ones as Cu4 in **figure S6**.

Figure 5. The construction of structural motif from the Yb (blue colored atoms) and Ga (green colored atom, others are shown with violet color) coordination atmospheres in $\text{Yb}_6(\text{CuGa})_{50}$ compound (S.G. $C2/m$)

Figure 6. Structural relation between the two compounds $\text{Yb}_6(\text{CuGa})_{50}$ and $\text{Yb}_6(\text{CuGa})_{51}$. Both structures originate from the same structure types, i.e., $\alpha\text{-Po}$, $\text{Hg}_{0.1}\text{Sn}_{0.9}$, and CaCu_5 . The additional distorted CsCl- structure type fragment along with three other structure types gives rise to $C2/m$ space group for $\text{Yb}_6(\text{CuGa})_{50}$. $\text{Hg}_{0.1}\text{Sn}_{0.9}$ and CaCu_5 structure type constitute two layers as A and B which sequentially construct ABAB type distorted $\text{Yb}_6(\text{CuGa})_{51}$ structure in $R\bar{3}m$ space group.

Figure 7 Structural evolution of Yb₆(CuGa)₅₁ from the same structure types- α -Po, Hg_{0.1}Sn_{0.9}, and CaCu₅. Layers A and B are constituted from Hg_{0.1}Sn_{0.9} and CaCu₅ structure types, sequential arrangement of which gives ABAB type distorted Yb₆(CuGa)₅₁ structure in $R\bar{3}m$ space group.

Figure 8. Structural evolution of Yb₆(CuGa)₅₀ from the same structure types. α -Po, Hg_{0.1}Sn_{0.9}, and CaCu₅ give rise to $C2/m$ space group upon the addition of distorted CsCl- structure type fragments shown in red color.

Figure 9. Temperature-dependent magnetic susceptibility (χ_m) and inverse magnetic susceptibility ($1/\chi_m$) of $\text{Yb}_6(\text{CuGa})_{51}$ at 1000 Oe.

Figure 10. X-ray absorption near edge spectrum (XANES) for $\text{Yb}_6(\text{CuGa})_{51}$. The dotted line represents the energy characteristic of divalent and trivalent Yb absorption at Yb L_{III} edges.

Figure 11. Resistivity (ρ) measured as a function of temperature. The low-temperature data has been fitted to the power law, $\rho = \rho_0 + AT^n$. The value of n obtained from the fit is shown in the figure.

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Complex Crystal Chemistry of $\text{Yb}_6(\text{CuGa})_{50}$ and $\text{Yb}_6(\text{CuGa})_{51}$ Grown at Different Synthetic Conditions

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Two new compounds in the Yb–Cu–Ga system $\text{Yb}_6(\text{CuGa})_{50}$ and $\text{Yb}_6(\text{CuGa})_{51}$ have been synthesized by metal flux crystal growth and high-frequency heating technique, respectively.