

# Single crystal growth of europium and ytterbium based intermetallic compounds using metal flux technique

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**Abstract.** This article covers the use of indium as a potential metal solvent for the crystal growth of europium and ytterbium-based intermetallic compounds. A brief view about the advantage of metal flux technique and the use of indium as reactive and non-reactive flux are outlined. Large single crystals of  $\text{EuGe}_2$ ,  $\text{EuCoGe}_3$  and  $\text{Yb}_2\text{AuGe}_3$  compounds were obtained in high yield from the reactions of the elements in liquid indium. The results presented here demonstrate that considerable advances in the discovery of single crystal growth of complex phases are achievable utilizing molten metals as solvents.

**Keywords.** Metal flux; intermetallics; crystal growth; europium; ytterbium.

## 1. Introduction

Intermetallics belong to the class of inorganic compounds containing exclusively two or more different kinds of metal (or metalloid) atoms as constituents. The difference between an intermetallic compound and a regular metal (e.g., a metallic element) is in the way the atoms are bonded. In metals, the bonding electrons distribute themselves throughout the material (i.e., the electrons are more delocalized), giving rise to predominantly non-directional bonding in the solid. Intermetallic compounds, on the other hand, maintain a slight ionic and covalent character (i.e., the electrons are rather localized), and the atomic bonding becomes more directional. The discovery of new physical effects in intermetallic compounds, such as intermediate valence, the Kondo effect, valence fluctuation, heavy-Fermion behaviour, superconductivity, structural transitions, etc., have stimulated much interest in these materials amongst the materials scientists.<sup>1–6</sup>

However, chemists have often found difficulties to synthesize the intermetallic compounds as it requires very high temperature conditions which are achieved by the use of induction heating and arc melting. Various approaches have been given for the investigation of the composition, crystal structure and properties of intermetallic compounds. A combined look at all the possible data available can help in understanding

the correlations between various characteristics exhibited by the intermetallic compounds. Intermetallic compounds with mixed valent rare earth ions are the most interesting ones. Every new compound discovered displays a novel situation in the properties (mentioned above). These properties are associated with the presence of an unstable electronic  $4f$ -shell, as some of the *RE* elements show two electronic configurations that are closely spaced in energy: for Ce, the magnetic  $\text{Ce}^{3+}(4f^1)$  and the non-magnetic  $\text{Ce}^{4+}(4f^0)$ , for Eu, the magnetic  $\text{Eu}^{2+}(4f^7)$  and non-magnetic  $\text{Eu}^{3+}(4f^6)$  and for Yb, the magnetic  $\text{Yb}^{3+}(4f^{13})$  and non-magnetic  $\text{Yb}^{2+}(4f^{14})$ . It is generally believed that, the stability of the different ground states depends strongly on the hybridization (interaction) strength between the magnetic  $4f$  electrons and the *s*, *p*, and *d* conduction electrons.<sup>7–9</sup> Under this consideration, the roles of the  $4f$  electron and  $4f$  hole can be interchanged and many interesting properties can be observed as mentioned above. However, the Ce-based intermetallic compounds have been more extensively studied compared to the Eu and Yb-based compounds due to the inherent difficulties in the sample preparation (high vapour pressure of Eu and Yb metals). Even though today there is a significant number of structural and physical characterizations of Eu and Yb compounds that exhibit many of the above mentioned intriguing properties, there have not been any reports of thorough investigations of  $\text{RE}_x\text{T}_y\text{X}_z$  (*RE* = Rare Earth, *T* = Transition metal, *X* = Terelide or Tetrelide). There are numerous interesting Eu and Yb-based intermetallic compounds synthesized by conventional techniques but

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they lack phase purity for their property studies. Here, we explain the vital role of metal flux method for growing the single crystals of interesting compounds both for their bulk and anisotropic properties and fishing new compounds in the sea of intermetallic chemistry.  $\text{EuGe}_2$ ,  $\text{EuCoGe}_3$  and  $\text{Yb}_2\text{AuGe}_3$  are the three examples explained briefly for the single crystal growth using metal flux technique.

## 2. Experimental

Extra care must be taken while performing exploratory reactions in a metallic flux, as the liquid metal must not react with the container and not evaporate during the synthesis. Because of this reason, the synthesis procedures (e.g., temperature profile) and containers vary, depending on the liquid metal. Generally, Al, Ga, In, Ge, Sn and Pb are the metals can be used as the flux for the single crystal growth of intermetallic compounds. Ge and Pb are not user friendly as they require high temperature to remove the flux by mechanical centrifugation and aluminum is highly reducing and react quickly with conventional container materials such as silica. Less reactive metals such as Sn, Ga, or In also react with silica if in contact for prolonged time and/or if the temperature is too high. A more attractive container material is alumina ( $\text{Al}_2\text{O}_3$ ), which is inert to Al, Sn, or Ga. In this case, alumina thimbles are used and are placed inside silica tubes, which are then sealed under vacuum conditions. Indium flux reactions have often been carried out in  $\text{ZrO}_2$  crucibles. A detailed selection of crucibles is outlined in the review by Kanatzidis *et al.*<sup>10</sup> After the reaction is over, product isolation is either done by recovering the solid ingot which contains the products embedded in the flux, or by immersing the entire thimble inside a flux-dissolving solution such as hydrochloric acid or aqueous sodium hydroxide. People have applied more versatile combinations of organic solvents with various oxidants such as  $\text{Br}_2$ ,  $\text{I}_2$ , peroxides to dissolve the excess metal flux.

Due to its low melting temperature of  $156.6^\circ\text{C}$ , indium is an ideal metal for use as a reactive flux (self-flux condition). It has widely been used for the synthesis and crystal growth of indium-rich binary and ternary intermetallics. In many cases, a slight excess of indium significantly increases the crystal growth. With indium there are again two types of reactions possible; those in which indium are incorporated into the products and those where it is acting strictly as an inactive solvent. Its low melting point makes indium convenient for reaction chemistry at relatively low temperatures and facilitates its removal during isolation.

In a typical experiment, the rare earth metal, the transition metal, p-block elements (normally telluride and selenide groups) and indium are mixed in an appropriate atomic ratio and placed in an alumina crucible which is sealed in an evacuated ( $10^{-3}$  torr pressure) silica tube to prevent oxidation. The sample is then heated over several hours to high temperature, normally up to  $1000\text{--}1100^\circ\text{C}$ , kept at that temperature for 2 h, and cooled down to  $700\text{--}850^\circ\text{C}$  over short period of times (5–6 h), kept for 24–48 h and finally cooled down to  $350^\circ\text{C}$ . At that temperature the excess indium is decanted in a centrifuge resulting in well-shaped single crystals with volumes up to  $1\text{ cm}^3$ . If only a small excess of indium is used for the self-flux technique, the melt-centrifugation technique cannot be applied. In this case it is better to dissolve the indium. A significant difference between intermetallics and binary and ternary stannides is that most stannides can resist 2N hydrochloric acid, intermetallics are often destroyed at this acidity. This problem can be avoided by removing the melt with diluted acetic acid.

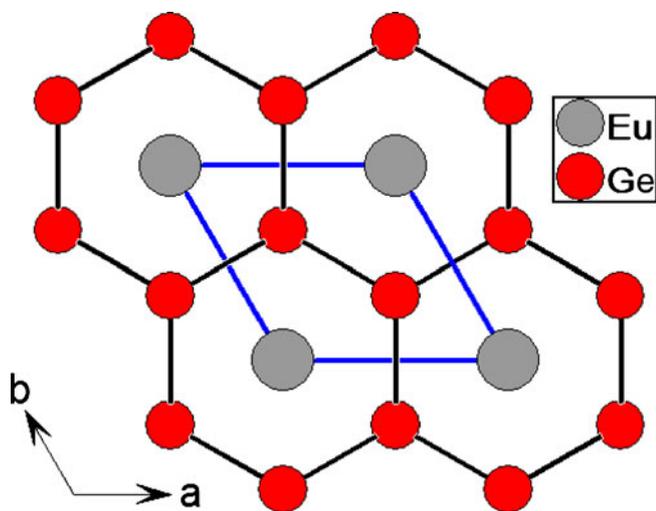
Indium has been exploited even less as a synthetic flux medium than aluminum and gallium. Recently In metal was employed as a solvent for the synthesis of germanides  $\text{Eu}_2\text{AuGe}_3$ ,<sup>11</sup>  $\text{YbGe}_3$ ,<sup>12</sup>  $\text{Yb}_4\text{TGe}_8$ ,<sup>5</sup>  $\text{Yb}_5\text{Ni}_4\text{Ge}_{10}$ ,<sup>13</sup> where In acts as a non-reactive flux, as well as a number of intermetallic compounds in which In gets incorporated into the products including  $\text{YbTIn}_5$  ( $T = \text{Co, Rh, Ir}$ ),<sup>14</sup>  $\text{YbPtIn}_4$ ,<sup>14</sup>  $\text{Yb}_7\text{Co}_4\text{InGe}_{12}$ ,<sup>15</sup>  $\text{Yb}_3\text{AuGe}_2\text{In}_3$ ,<sup>16</sup>  $\text{YbAu}_2\text{In}_4$ ,<sup>17</sup>  $\text{Yb}_2\text{Au}_3\text{In}_5$ .<sup>17</sup>

In this paper, we have used In as non-reactive flux for the crystal growth of  $\text{EuGe}_2$ ,  $\text{EuCoGe}_3$  and  $\text{Yb}_2\text{AuGe}_3$  compounds. Semi-quantitative microprobe analyses of the samples were performed with a Hitachi S-3400 scanning electron microscope (SEM) equipped with an energy dispersive X-ray analyzer and phase identity and purity of samples were determined by powder XRD experiments carried out on a diffractometer using  $\text{Cu K}\alpha$  radiation. We have omitted the single crystal structure refinement and physical property studies which will be published in near future.

## 3. Results and discussion

### 3.1 $\text{EuGe}_2$

$\text{EuGe}_2$  crystallizes in the trigonal space group  $P\bar{3}m1$  with the  $\text{CeCd}_2$ -structure type. Its structure can be formally derived from the hexagonal  $\text{AlB}_2$ -structure type by a strong puckering of the hexagonal layers (figure 1).  $\text{EuGe}_2$  was already prepared by Bobev *et al.*<sup>18</sup> as polycrystalline material by high temperature (above  $822^\circ\text{C}$ ) ceramic method. To minimize the loss



**Figure 1.** Projection of the trigonal  $\text{EuGe}_2$  structure along the  $c$  axis.

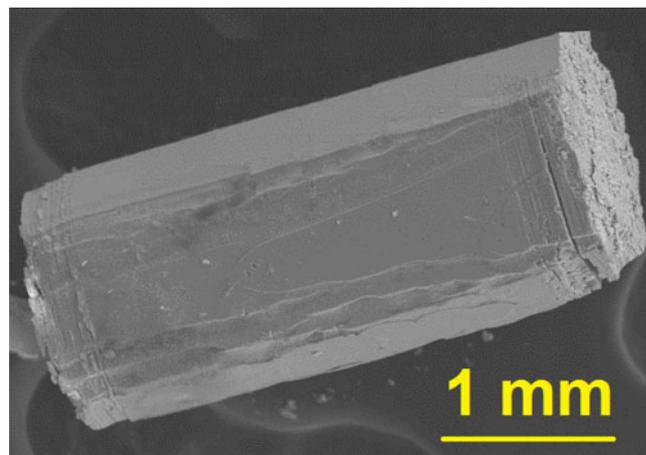
of elemental Eu during the heating process, they performed the reactions in weld sealed Ta-tubes. Under these conditions, the reaction outcome contained considerably less unreacted elemental Ge, but the reaction product was always contaminated with  $\text{EuGe}$  and  $\text{TaGe}_2$ . One of the problems faced during the sample preparations, the reaction products were inhomogeneous powders and/or polycrystalline pieces. Further, arc-melting of the as-cast products and subsequent annealing for prolonged periods of time at ca.  $650^\circ\text{C}$  were also explored, but failed to produce quantitative yields and/or good quality of single crystals. Therefore, all property measurements discussed in their report were carried out on polycrystalline ingots of  $\text{EuGe}_2$ .

The presence of impurities is one of the main concerns toward the physical property measurements of the  $\text{EuGe}_2$  compounds. Secondly, it is very important to produce large single crystals to study anisotropic behaviour in this compound. For these reasons we have attempted to grow the single crystals of  $\text{EuGe}_2$ . The single crystals of  $\text{EuGe}_2$  were first discovered in a reaction that was initially designed to optimize the indium flux synthesis of the  $\text{Eu}_2\text{AuGe}_3$  phase. Later, we established the growth of  $\text{EuGe}_2$  single crystals by combining 1 mmol of europium metal, 2 mmol of germanium and 45 mmol of indium in an alumina crucible under an inert nitrogen atmosphere inside a glove-box. The crucible was placed in a 13 mm fused silica tube, which was flame sealed under a vacuum of  $10^{-4}$  Torr, to prevent oxidation during heating. The reactants were then heated to  $1000^\circ\text{C}$  over 10 h, maintained at that temperature for 5 h to allow proper homogenization, followed by cooling to  $850^\circ\text{C}$  in 2 h and held there for 48 h. Finally, the sample was allowed to slowly cool

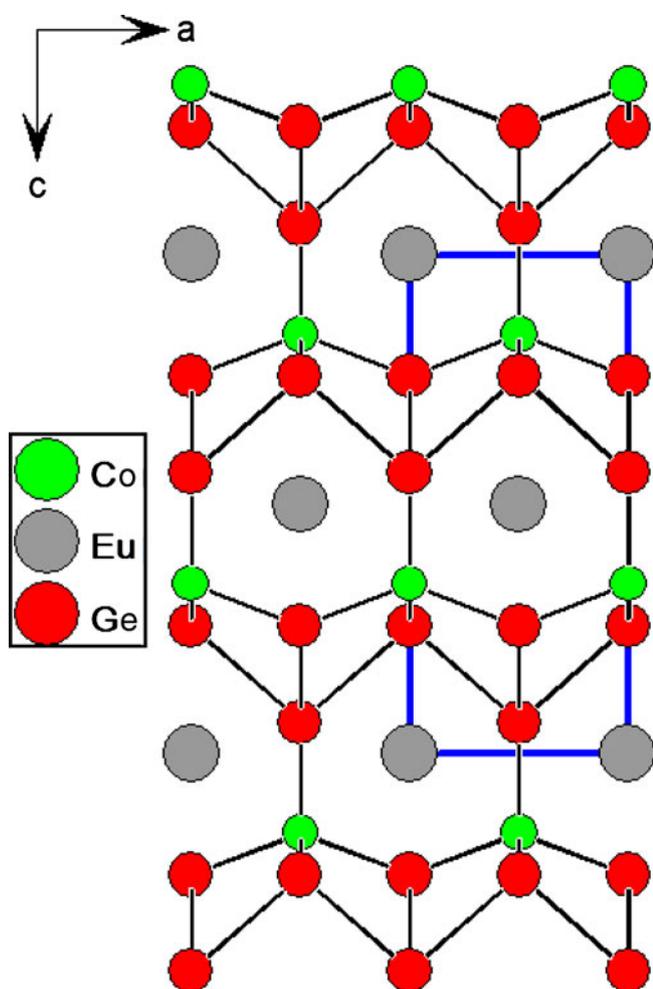
to  $50^\circ\text{C}$  in 48 h. The reaction product was isolated from the excess indium flux by heating at  $350^\circ\text{C}$  and subsequently centrifuging through a coarse frit. Any remaining flux was removed by immersion and sonication in glacial acetic acid for 48 h. The final crystalline product was rinsed with water and dried with acetone. This method produced the target compound with  $\sim 99\%$  purity and in a yield more than 50% on the basis of the initial amount of Eu metal used in the reaction. Main side products were very small amounts of recrystallized Ge and residual In metal flux. The light gray rod shaped single crystals of  $\text{EuGe}_2$ , which grow as metallic silvery rods up to 4 mm in length were stable in air and no decomposition was observed even after several months. A typical single crystal of  $\text{EuGe}_2$  is shown in figure 2. Single crystals have metallic lustre. Elemental analysis and powder XRD confirm the formation of  $\text{EuGe}_2$ .

### 3.2 $\text{EuCoGe}_3$

The germanium-rich  $\text{EuCoGe}_3$  crystallizes with the noncentrosymmetric  $\text{BaNiSn}_3$  type structure, an ordered variant of the  $\text{BaAl}_4$  ( $\text{ThCr}_2\text{Si}_2$ ) type. A projection of the  $\text{EuCoGe}_3$  structure is presented in figure 3. Polycrystalline samples were prepared by Venturini *et al.*<sup>19</sup> by melting appropriate amounts of the constituent elements at high temperature. At the present time, the structural studies have been performed only with X-ray powder diffraction technique. The X-ray diffraction experiments confirmed that  $\text{EuCoGe}_3$  is tetragonal  $\text{BaNiSn}_3$ -type ( $I4mm$ ) structure with  $a = b = 4.325(4)$  Å and  $c = 9.894(9)$  Å. The single crystals of  $\text{EuCoGe}_3$  were obtained by combining 3 mmol of europium metal, 2 mmol of cobalt, 6 mmol of germanium and



**Figure 2.** Typical large single crystal of  $\text{EuGe}_2$  grown from In metal flux.

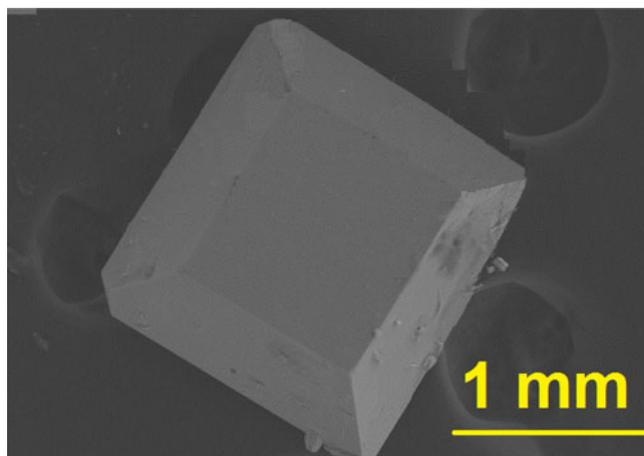


**Figure 3.** Projection of  $\text{EuCoGe}_3$  structure along the  $b$  axis.

45 mmol of indium in an alumina crucible under an inert nitrogen atmosphere inside a glove-box. The synthesis conditions used were same as for  $\text{EuGe}_2$  compound. Several crystals of  $\text{EuCoGe}_3$ , which grow as metallic silvery cubic prismatic shape (typical single crystal is shown in figure 4), were carefully selected for elemental analysis. The other product observed from the synthesis is rod shaped  $\text{EuGe}_2$ . The crystals were stable in air and no decomposition was observed even after several months. Single crystals have metallic lustre. SEM/EDS analysis and powder XRD confirm the formation  $\text{EuCoGe}_3$  compound. A detailed single crystal XRD and property studies will be done in near future.

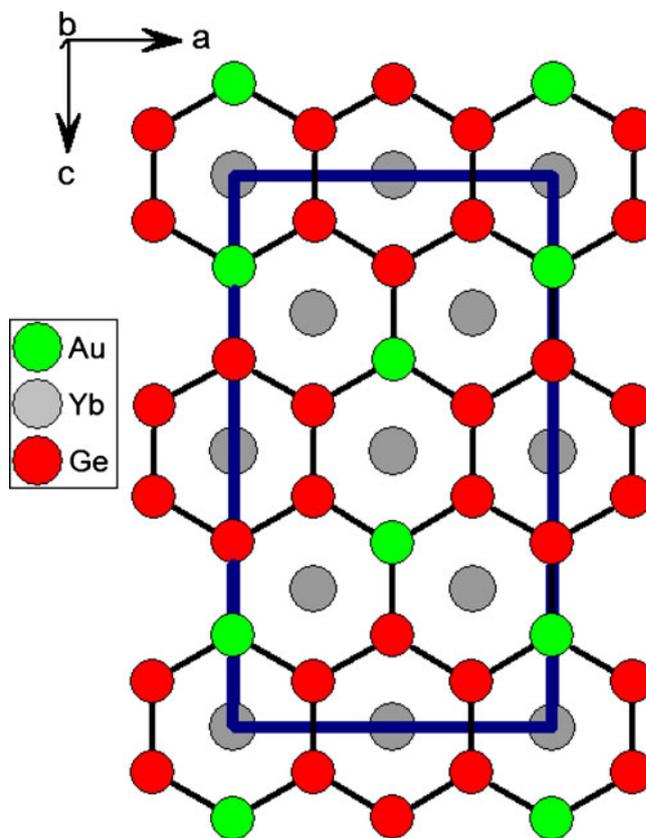
### 3.3 $\text{Yb}_2\text{AuGe}_3$

Intermetallics with the general formula  $\text{RE}_2\text{AuGe}_3$  crystallize with a superstructure of the well-known  $\text{AlB}_2$  family. Several compounds with composition

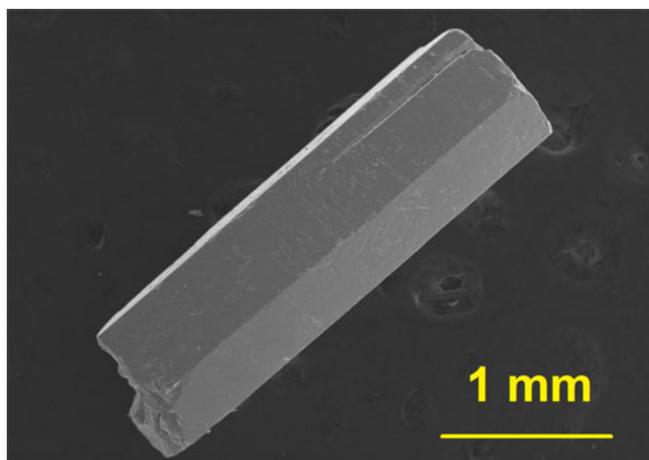


**Figure 4.** Typical cubic prismatic single crystal of  $\text{EuCoGe}_3$  obtained from In metal flux.

2:1:3 were reported within different complicated superstructures. These have ordered arrangements within the hexagonal networks, and the simplest ordering variants are  $\text{U}_2\text{RuSi}_3$ ,<sup>20</sup>  $\text{Ce}_2\text{CoSi}_3$ ,<sup>21</sup> and  $\text{Eu}_2\text{PdSi}_3$ .<sup>22</sup> Depending on the valence electron concentration and geometrical restraints, such compounds show different ordering patterns and stacking sequences. Recently we have



**Figure 5.** View of the  $\text{Yb}_2\text{AuGe}_3$  structure approximately along the  $b$  axis. Ytterbium atoms are embedded in the two-dimensional hexagonal  $[\text{AuGe}_3]$  networks.



**Figure 6.** Large sized single crystal of  $\text{Yb}_2\text{AuGe}_3$  grown from In metal flux.

synthesized a novel compound  $\text{Eu}_2\text{AuGe}_3$ <sup>23</sup> using In as metal flux crystallized in the  $\text{Ca}_2\text{AgSi}_3$  structure type (figure 5) at room temperature and showed a phase transformation to the superstructure at lower temperature (130 K). This has motivated us to check the existence of its counterparts and started with ytterbium element.  $\text{Yb}_2\text{AuGe}_3$  was obtained as large single crystals in high yield from a reaction of the elements in liquid indium. The grey rod shaped single crystals of  $\text{Yb}_2\text{AuGe}_3$  were obtained from the flux reaction (figure 6). Our preliminary single crystal data at room temperature suggests that  $\text{Yb}_2\text{AuGe}_3$  crystallizes with the  $\text{Ca}_2\text{AgSi}_3$  type, space group  $Fmmm$ , an ordered variant of the  $\text{AlB}_2$  type:  $a = 8.5124(17) \text{ \AA}$ ,  $b = 14.730(3) \text{ \AA}$ ,  $c = 8.4995(17) \text{ \AA}$ . The gold and germanium atoms build up slightly distorted graphite-like layers which consist of  $\text{Ge}_6$  and  $\text{Au}_2\text{Ge}_4$  hexagons, leading to two different hexagonal-prismatic coordination environments for the europium atoms. The elemental analysis of this compound with SEM/EDS gave the atomic composition which is in excellent agreement with the results obtained from the single crystal refinement data.  $\text{Yb}_2\text{AuGe}_3$  shows metallic luster, is stable and no decomposition was observed even after several months. A detailed property studies on separated single crystals of  $\text{Yb}_2\text{AuGe}_3$  will be published in near future. Powder XRD data of crushed single crystal of  $\text{Yb}_2\text{AuGe}_3$  could be indexed on the basis of an orthorhombic unit cell.

#### 4. Conclusions

Metal fluxes have been proved as a better technique for the single crystal growth of Eu and Yb-based compounds compared to the conventional techniques like

arc melting and high frequency induction furnaces because of the low vapour pressure of Eu and Yb. The other advantages of metal flux (solvent) are that it can enhance diffusion of the elements and lower the reaction temperatures. Though in this article, we have focused mainly on the single crystal growth of  $\text{EuGe}_2$ ,  $\text{EuCoGe}_3$ ,  $\text{Yb}_2\text{AuGe}_3$ , these materials can show a variety of interesting phenomena and applications.

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