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A review on the synthesis, crystal growth, structure and physical properties of rare earth based quaternary intermetallic compounds

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ABSTRACT

This review highlights the synthesis and crystal growth of quaternary intermetallic compounds based on rare earth metals. In the first part of this review, we highlight briefly about intermetallics and their versatile properties in comparison to the constituent elements. In the next part, we have discussed about various synthesis techniques with more focus on the metal flux technique towards the well shaped crystal growth of novel compounds. In the subsequent parts, several disordered quaternary compounds have been reviewed and then outlined most known ordered quaternary compounds with their complex structure. A special attention has been given to the ordered compounds with structural description and relation to the parent binary and ternary compounds. The importance of electronic and structural feature is highlighted as the key roles in designing these materials for emerging applications.

1. Introduction

The intermetallic compounds are solid state materials exclusively containing at least two or more than two different metals (sometime metalloids). Intermetallics are also unique compared to the metals in terms of their bonding features. The bonding electrons are more delocalized in metals and distribute themselves throughout the material resulting in predominantly nondirectional bonding in the solid. On the other hand, the atomic bonding in intermetallic compounds is more directional, which means the electrons are more localized having slight ionic and covalent character. Chemists often find difficulty in understanding some very basic characteristics of intermetallic compounds mostly their compositions, bonding, and assignment of oxidation states for individual atoms. Because of this, the synthetic solid state chemistry community has given more attention to the growth of the materials such as oxides, ceramics, carbides, borides, pnictides, chalcogenides, or halides. Even then, intermetallics are considered to be an important class of materials with wide range of applications in modern functional, constructional and technological industries. The applications are broadly classified into shape memory alloys, permanent magnets, magnetic recording materials, superconductors, battery materials, light weight alloys for aerospace and other vehicle construction, catalysts, solders, thermoelectric materials and so on [1–9].

In general, all crystalline compounds can be classified as ordered and disordered compounds based on the fact that whether each crystallographic site is occupied solely by a single constituent atom or have mixed positions shared statistically between two atoms respectively. Both of these arrangements are crucial in generating novel ternary and quaternary structure types from the corresponding binary structure, which effectively acts as a structural template for those compounds. Majority of the intermetallics reported are binary compounds as they are relatively easier to synthesize and holding simple structural analysis. Most of these compounds are reported in the crystal structure types of the constituent metals or ordered types of the same. The crystallographic details of all these compounds are available in Inorganic Crystal Structure Database [10] and Pearson's crystal data [11], and the well established phase diagrams accessible via Pauling phase diagram databases. It is a well known fact that many of the metals are known to exist in different modifications at high temperature and high pressure leading to a wide variety of structures, chemical bonding and physical properties, which motivated the chemists to focus on the binary compounds for their diversity in structure and physical properties. This has been exemplified with a plethora of literature reports available for several decades. In going from binary to ternary and quaternary compounds one ends up with incredible number of new phases and sometime new structure types. During last two decades, plenty of new ternary structure types were reported, many of them were contributed by our group as well [12–22].

Intermetallic materials often exhibit different physical properties such as spin density wave ordering, thermoelectricity, topological

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insulating properties, first-order phase transitions, metamagnetic transitions, high magnetic anisotropy, high magnetic moments and Curie temperature, high spin polarization and various semiconducting properties [23–30]. This diversity renders intermetallics as attractive materials not only for exploring fundamental aspects of matter but also raises interest for the versatile modern technological applications. The electronic ground state can be tuned or modified by making them in complex structures. For example, several intermetallic compounds contain group 13 and/or group 14 elements as one of the constituents. The physical properties of commercial aluminum or silicon can be improved by adding rare-earth (*RE*) or transition (*T*) metals. An attempt in modifying the physical properties may result in the formation of both known as well as yet unexplored multinary intermetallic compounds within the aluminum or silicon matrix. It is a demanding challenge to optimize the bulk materials as possible multinary compounds. The addition of *RE* and/or *T* metals, mostly resulted in complex structures and interesting magnetic and electronic behavior. The key tool in the rational design of intermetallic compounds is the knowledge and control of the properties, and whether they are dominated by intrinsic factors (e.g. electronic structure and anisotropic properties) or by extrinsic factors (e.g. structural order, phase dynamics). These two parameters become complicated but more interesting when these classes of materials are made up of constituents with diverse chemical characteristics.

In going from binary to ternary and then to quaternary compounds, complexity of the crystal structures proportionate. Therefore the synthesis and growth of single crystals are crucial to understand the precise structures. Growing high quality single crystals is of utmost importance not only for proper structural characterization but also for the better physical property measurement as it is well known that pellets made up of polycrystalline compound contain microscopic grain boundaries which may affect the transport properties of the system. Moreover, synthesis of a high quality single crystal is the only way for the measurement of asymmetric physical property. Synthesis of single crystals using different methods is mainly classified into three groups, namely gas–solid, liquid–solid and solid–solid processes, depending on mixing of different phases. The liquid–solid process is one of the most popular and oldest techniques. Depending upon medium, liquid–solid process is further divided into different subgroups. High quality single crystals can be grown from melts method at large scale in the field of elemental semiconductors, metals, oxides, halides and chalcogenides.

In this review, we have detailed the synthesis, crystal growth and crystallographic structures of quaternary *RE* based compounds. *RE* elements (atomic number 57–71) having electronic configuration (Xe)$4f^{0-14}5d^{0-1}6s^2$ with partially filled 4*f* orbital displaying the trivalent state except cerium, europium, and ytterbium. *RE* elements are characterized by localized 4*f* electrons, which are shielded by the outer $5s^2$–$5p^6$ electrons [31,32] and to some extent by 5*d*–6*s* electrons. *RE* based binary, ternary and quaternary compounds have been investigated extensively in last few decades due to their versatile application in the field of magnetic, and superconducting materials as well as in hydrogen storage. Recently, *RE* based intermetallic compounds have been attracting much attention because of their versatile structural and physical properties such as intermediate valency [33], spin glass behavior [34], structural phase transition [19], magnetocaloric effect [35], giant magnetoresistance [36], superconductivity [37] and zero thermal expansion [13]. The review has been written from the synthetic solid state chemist's point of view. In this article, we have tried our best to provide an overall glimpse of crystallographic and structural description of almost all quaternary intermetallic compounds. The crystal structures are represented using the cif files taken from the PCD and ICSD databases and briefly discussed about the doped or substituted ternary compounds with the assumption that they are pseudo quaternary compounds. This review provides a broad literature review on the ordered quaternary compounds and explained the crystal structure of each compound briefly along with the comparison to the parent binary or ternary compound. We also explained the preliminary physical properties of these compounds reported so far. Interested readers may use the cited literature for deeper information.

2. Synthesis

One of the criteria for the successful synthesis of intermetallic compounds is better diffusibility of the constituent elements. At least one of them should reach adequate diffusion rate in the range of 10^{-12} cm^2/s. Tammann rules state that at least one of the elements should reach 2/3 of the melting point to enable diffusion at reasonable time scale [38]. Traditionally, ceramic method is known as the mostly used for the synthesis of intermetallic compounds. The constituent elements taken in a quartz tube or any other ampoules and heat them at high temperature in a furnace over a period of time. Later, the conventional techniques such as arc melting and high frequency induction heating have been used to reduce synthesis time scale with better diffusion of the reactants [26]. Although there are several advantages of these methods, confined in the synthesis of kinetically stable compounds and well shaped single crystals. For the better understanding of the crystal structure of the compounds, regular shaped single crystal growth is crucial. Since kinetic controls by these methods are limited, the tactic selection of a particular composition for synthesis is nearly not possible. However, these methods are often used for the bulk production of the compounds after establishing the crystal structure.

2.1. Metal flux method

The crystal growth of materials is one of the prime research focus in the field of solid state chemistry for the anisotropic physical property measurements and device fabrications in various technological applications. In the recent years, molten metals and metal salts have been employed for the growth and development of several known and novel compounds. Molten salts have been generally used for the growth of chalcogenides and oxides, but, the molten metal flux technique has been proved as an outstanding tool for the discovery of new materials in the intermetallic family due to their enhanced diffusibility power of the elements in the solvent and the lower reaction temperatures. The latter allows better kinetic control that gives more flexibility to adopt stable compound with novel compositions and atomic arrangements in the structure [39]. The details on the physics and chemistry of the metal flux technique have been outlined in a recent review article [40].

The application of molten metals such as Al, Ga, In, Sn and Pb used as solvents to carry out the exploratory synthesis of complex intermetallic quaternary compounds led to the discovery of a number of new multinary phases [41–51]. The ability of these metals to exist as solvent over a wide range of temperature efficiently explored in the crystal growth of *RE* based intermetallics. The interest in the reactivity and phase formation of a few quaternary compounds due to ubiquitous incorporation of these metals into the system and reaction product strongly depends on *RE* and is also significantly more sensitive to the reaction conditions. These low-melting molten metal fluxes help in facilitating the diffusion of the elements in its solution at temperature lower than the melting point of the constituent metals. Optimizations of the