Survey of new materials by solid state synthesis under external fields: high-pressure synthesis and microwave processing of inorganic materials

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The most common preparative method for inorganic solids is solid state reaction of constituent materials. Since the solid state reaction is usually performed at high temperature for a long heating duration, almost all the products are thermodynamically stable. During the long history of solid state chemistry and materials science, an enormous number of binary and ternary equilibrium phase diagrams were constructed and it seems like there is no hope to find out new materials those exhibit fascinating functionality. By applying external fields to solid state reaction systems, however, it has become possible to synthesize new compounds those do not exist in the equilibrium phase diagrams. In this article, synthesis of inorganic materials under high-pressure and microwave electromagnetic fields is reviewed. The scope of this review covers, but is not limited to, effects of external fields (high-pressure and microwave electromagnetic wave) on the formation of new compounds and structures those can not be prepared by conventional synthetic routes.

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1. Introduction

Design and synthesis of new inorganic materials is one of the major concerns in current materials science and solid state chemistry. The discovery of new compounds and/or new structures often open the way for breakthrough in materials science as demonstrated in high-temperature superconductors and rare-earth magnets. In most cases, however, the discovery of new materials is largely empirical (actually “product of chance”) because it is difficult to predict and design a new material with desirable functionality before the discovery.

It is obvious that understanding of the relationship among structure, bonding and physical properties is the essential part in solid state science. Recent development in computer chemistry enables us to predict the physical properties of a hypothetical chemical compound, leading to realize the “materials design” for a specific functionality. It should be noted, however, that the synthesis of the designed materials is more important to actually realize the “materials design” otherwise the design will be just wishful thinking.

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There are many preparative methods for inorganic solid materials and the choice of synthetic routes is one of the great challenges in materials processing. Among them, solid state reaction (ceramic method or powder metallurgical processing) is the simplest and traditional method commonly used to prepare inorganic solids. Since the solid state reaction is performed by high-temperature heat treatment for prolonged periods, thermodynamically stable products are obtained in general. If we want to make a new phase (to realize the materials design) that is thermodynamically unstable or metastable, we have to introduce “non-equilibrium reaction field” to the chemical reaction system.

Many new phases can be prepared by a variety of chemical reactions under specific external fields. By applying external fields to solid state reaction systems, one may obtain non-equilibrium new phases or structures even in the case of simple binary component systems. In this review article, recent achievement in high-pressure synthesis and microwave processing of inorganic materials is broadly discussed.

2. High-pressure synthesis

High-pressure synthesis still appears to be an important tool for the synthesis of advanced new inorganic materials.
Historically, high-pressure synthesis has been used to synthesize rock-forming minerals in the field of geoscience because the Earth’s interior is in high-pressure and high-temperature condition. Moreover, another important usage of high-pressure technique is the synthesis of covalent-bonded super-hard materials, starting with diamond and cubic boron nitride (c-BN) by GE group in 1955 and 1957, respectively.

Nowadays, a large number of new materials have been synthesized and the current interest is focused on the synthesis of super-hard materials, wide-gap semiconductors, high-T_c superconductors, and various ferroelectric and magnetic materials. The major characteristics and the advantages of high-pressure synthesis are as follows:

1) Pressure-induced phase transitions of ambient pressure phases to the dense-packed structures.
2) Compound formations with new chemical formulae those do not exist in the equilibrium phase diagrams at ambient pressure.
3) Synthesis avoiding decomposition and/or sublimation of volatile reactants.
4) Chemical reactions greatly facilitated by applying pressure.

These characteristics enable us to synthesize various new materials, especially intermetallic compounds between transition metal and metalloid system, and the compounds within metalloid group, because metalloid elements at ambient pressure have relatively open structures and some of them exhibit high vapor pressure. From this point, high-pressure synthesis of intermetallic compounds and covalent-bonded materials containing metalloid elements were extensively studied in our laboratory.

Generally high-pressure synthesis is performed in the following order. At the 1st step, the reactant (e.g. powder mixture) is encapsulated and subjected to high-pressure before heating. Then the specimen is heated to a synthetic temperature under the desired pressure condition. After the reaction, the specimen is quenched to room temperature prior to the release of the applied pressure. The applied pressure is released finally after quenching. Most of high-pressure phases can be metastably retained at ambient condition in this way.

Several types of apparatus, piston-cylinder, belt, and multi-anvil, have been used for high-pressure synthesis above 1 GPa. Among them, the belt-type apparatus has relatively large cell volume and widely used for the material synthesis under pressure range of 3–8 GPa. In our study, the belt-type apparatus has been used for the synthesis of various materials described below. The detailed operating procedure, as well as the cell assembly for high-pressure synthesis, is described in our earlier paper.

2.1 Survey of new materials in transition metal-metalloid system

Intermetallic compounds in transition metal-metalloid system have been widely investigated because of their variety of electrical, magnetic, and combined electro/magnetic properties and their practical use in solid state devices. The common preparative method for intermetallic compounds is the direct reaction of elemental components. One may expect that the application of high-pressure greatly facilitates the reaction because the phase formation from the elemental components generally accompanies a large volume decrease. In our extensive study, many binary intermetallic compounds have been synthesized under high-pressure/temperature conditions. In many cases, formation of new compounds resulted from the closed reaction field avoiding the loss of volatile components, stabilization of crystal structures to a certain extent, and changes in bonding nature from non-metallic character to metallic one.

It is somewhat difficult to predict the formation of new intermetallic compounds under high-pressure due to their complicated structure-determining factors. In many intermetallic phases, major structure-determining factors are atomic size and valence electron concentration of the constituents, those are dramatically changed by applying high-pressure.

Metalloid elements themselves change their bonding character from covalent one to metallic one under high-pressure. This leads to changes in binary metal-metalloid phase diagrams to alloy-like ones under high-pressure condition. A good example can be found in the binary Ag–Ge system. The equilibrium phase diagram of Ag–Ge system is a simple eutectic-type with no intermediate phases at ambient pressure. However, a new intermediate phase (η-Ag3Ge), that can be regarded as the Hume-Rothery phase, appeared at elevated pressure (4–7 GPa).

In our study, four new manganese germanides, Mn3Ge, Mn5Ge2, Mn7Ge3, and Mn9Ge8, could be synthesized under high-pressure condition of 4–6 GPa in the binary Mn–Ge system, although six intermediate phases, Mn3.4Ge, Mn6Ge2, Mn7Ge3, Mn9Ge5, Mn11Ge7, and Mn13Ge8, are known to exist and no intermediate phases in the Ge-rich portion in the equilibrium phase diagram at ambient pressure (Fig. 1). It should be noticed that the occurrence of intermediate phases in the Ge-rich portion under high-pressure is obviously due to the increase in metallic character of germanium atoms. Similarly, other binary transition metal germanides (VGe2, Cr3Ge7, CoGe4, and...
NiGe$_2$)$_{9,11,13}$ antimonides (MnSb$_2$ and Mn$_3$Sb)$_{14,15}$ and mixed gallides/antimonides (MnGa$_2$Sb$_2$ and CrGa$_2$Sb$_2$)$_{16,17}$ were successfully synthesized under high-pressure condition. It is also notable that, through these synthetic studies, we found the general tendency that the formation of new phase under high-pressure easily occurs at the composition near the eutectic point in the equilibrium phase diagram at ambient pressure condition. Among these phases, some compounds exhibit metallic ferromagnetic behavior with the Curie temperatures above room temperature. The detailed of their magnetic characterization is reviewed in the next section.

Little is known on the pressure-induced phase transitions of intermetallic phases as compared to ionic and covalent materials. Transition metal pnictides and chalcogenides show a variety of polymorphic transitions under high-pressure. For example, many MX$_2$ (M: transition metal, X: pnictogen or chalcogen) compounds undergo pressure-induced phase transitions from the marcasite- or arsenopyrite-type to the pyrite-type structures.$^{18,19}$ We have found the another type of pressure-induced transition in NiSb$_2$, from the low-pressure marcasite-type to the high-pressure pararammelsbergite-type structure.$^{20}$ Both type of phase transitions can be explained by effective packing of MX$_6$ octahedra. The most effective packing in this series of structures is achieved in the pyrite-type in which MX$_6$ octahedra connect with adjacent octahedra by corner-sharing only, while the marcasite-type consists of edge-sharing octahedra. The pararammelsbergite-type possesses intermediate structure composed of mixed corner- and edge-sharing octahedra (Fig. 2).

In literatures, the opposite type of phase transition, pressure-induced pyrite-type to marcasite-type transition was reported in MnS$_2$ and MnTe$_2$ that can be explained due to high-spin to low-spin transition of Mn$^{3+}$ (3d$^5$), which accompanies a large volume decrease.$^{21,22}$ Another representative of phase transitions in this family can be seen in CrSb$_2$. At ambient pressure, CrSb$_2$ crystallizes into the marcasite-type structure and is an antiferromagnetic semiconductor ($T_N = 275$ K) with the localized high-spin 3d$^5$ electron configuration.$^{24}$ It transforms to the CuAl$_2$-type structure above 5.5 GPa.$^{23}$ In the low-pressure marcasite form, each chromium atoms are octahedrally coordinated by six antimony atoms, while in the high-pressure form, each chromium atoms are coordinated by eight antimony atoms to form a square antiprism and additionally two chromium atoms to form Cr–Cr–Cr–Cr linear chains along the c-axis. Consequently, the phase transition from the marcasite-type to the CuAl$_2$-type structure accompanies a large volume decrease and the change in bonding nature from the mixed ionic/covalent to metallic. The high-pressure phase of CrSb$_2$ can metastably be retained to ambient condition and exhibits an itinerant electron ferromagnetic behavior with the Curie temperature of 160 K.$^{23}$ In summary of this part, pressure-induced phase transitions in transition metal dipnictides and dichalcogenides family are schematically drawn in Fig. 2.

### 2.2 New ferromagnetic compounds

Synthesis of new magnetic materials is one of the major concerns in chemical processing of functional materials. In the last decade a lot of new magnetic materials have been studied in the viewpoints of hard magnets, magnetocaloric materials, magnetic semiconductors, and strongly correlated materials. It is only four elements (iron, cobalt, nickel, and gadolinium) out of nearly 70 metallic elements that are ferromagnetic at room temperature, however, other transition metals (especially chromium and manganese) can be converted to ferromagnetic by alloying with other metals or metalloids.

Survey of new ferromagnetic materials in 3d transition metal-metalloid system has been conducted using high-
pressure synthesis technique. Seven new ferromagnetic compounds, \( \text{Cr}_4\text{Ge}_7 \) \( (T_C = 270 \text{ K}) \),\(^{11,12} \) \( \text{Cr}_2\text{Sb}_2 \) \( (T_C = 160 \text{ K}) \),\(^{23} \) \( \text{CrGa}_2\text{Sb}_2 \) \( (T_C = 345 \text{ K}) \),\(^{17} \) \( \text{Mn}_3\text{Ge} \) \( (T_C = 400 \text{ K}) \),\(^{7} \) \( \text{Mn}_3\text{Sb} \) \( (T_C \approx 200 \text{ K}) \),\(^{13} \) \( \text{MnGe}_4 \) \( (T_C = 340 \text{ K}) \),\(^{9} \) and \( \text{MnGa}_2\text{Sb}_2 \) \( (T_C = 310 \text{ K}) \),\(^{16} \) have been successfully synthesized and their structure and magnetic properties have been characterized.

Among these compounds, \( \text{MnGe}_4 \) and its analogues, \( \text{MnGa}_2\text{Sb}_2 \) and \( \text{CrGa}_2\text{Sb}_2 \), make a unique class of materials composed of one-dimensional linear chain of magnetic atoms. **Figure 3** shows the crystal structure of \( \text{MnGe}_4 \) and its isoelectronic analogue, \( \text{MnGa}_2\text{Sb}_2 \).\(^{16} \) Each manganese atoms are cubically coordinated by eight metalloid atoms and additionally two manganese atoms to form \(-\text{Mn}–\text{Mn}–\text{Mn}–\) linear chain, that is believed to cause a ferromagnetic interaction in this class of materials. All of these three compounds exhibit ferromagnetism at room temperature even though the percentage of the magnetic atom content (Mn or Cr) is 20% in the chemical composition.

Ferromagnetic behavior of these compounds can be well explained by an itinerant-electron ferromagnetic behavior and the observed small magnetic moment (1.2 \( \mu_B/\text{Mn} \) for \( \text{MnGe}_4 \), 1.47 \( \mu_B/\text{Mn} \) for \( \text{MnGa}_2\text{Sb}_2 \), and 1.6 \( \mu_B/\text{Cr} \) for \( \text{CrGa}_2\text{Sb}_2 \)) reflects a low-dimensional character of 3\( d \) band in this family of compounds.\(^{16,17} \) Similar low-dimensional character is also observed in the Cu\_2Sb-type Mn-compounds, \( \text{Mn}_2\text{Sb} \), \( \text{MnAlGe} \), \( \text{MnGaGe} \), and \( \text{MnZnSb} \).\(^{25-27} \) It should be pointed out that the MnGe\_4-type structure is closely related to the Cu\_2Sb-structure; that is, MnGe\_4-type structure can be derived from the Cu\_2Sb-type structure with the removal of a half of linear chains as schematically depicted in **Fig. 4**, leading to one-dimensional character of the metal chain as compared to two-dimensional net plane of metals in the Cu\_2Sb-type compounds. **Figure 5** represents the relation between Curie temperature and the Mn–Mn interatomic distance within \(-\text{Mn}–\text{Mn}–\text{Mn}–\) linear chains of the MnGe\_4-type compounds, together with those of the Cu\_2Sb-type compounds. One can see a universal curve indicating that the ferromagnetic interaction in these compounds strongly depends on the Mn–Mn interatomic distance in the magnetic linear chains.

It should be pointed out that the ferromagnetism in MnGe\_4-type compounds recently began to attract much attention in relation to the ferromagnetism in transition metal-doped \( 13–15 \) and \( 12–16 \) semiconductors (diluted magnetic semiconductors, DMSs) for their possible application to spintronics devices.\(^{28-33} \) Survey of new materials with these closely related structures may help the furt-
Further discussion on understanding the magnetic properties of intermetallic compounds containing low-dimensional metal chains and/or plane.

2.3 Macro-tetrahedral compounds

High-pressure synthesis generally facilitates phase formations accompanying the increase in coordination number of atoms. For example, three-fold coordinated graphite and hexagonal boron nitride (h-BN) transform to tetrahedrally coordinated diamond and cubic boron nitride (c-BN), respectively. Similarly, high-pressure synthesis is favorable for the synthesis of compounds containing tetrahedrally coordinated “light” elements.

At ambient pressure, $\text{B}_2\text{S}_3$, $(\text{BS}_2)_n$, and $\text{B}_8\text{S}_{16}$, are known to form in the binary boron-sulfur system.\(^{34)-36}\) These boron sulfides are made up of planar BS$_3$ triangles composed of sp$^2$-hybridized boron atoms. It is expected that new compounds composed of sp$^3$-hybridized tetrahedral boron atoms would be stabilized under high-pressure condition.

During our extensive study, five new compounds, BS, $\text{B}_2\text{S}_3$ (H.P.), $\text{CaB}_2\text{S}_4$-I, $\text{CaB}_2\text{S}_4$-II, and $\text{CuBS}_2$, could be synthesized and metastably retained to ambient condition.\(^{37)-40}\) Among them, boron monosulfide (BS), exhibiting a wide-gap semiconducting behavior with a band gap of 3.4 eV, has a layered structure comprised of units built up from B–B pairs located inside the anti-prism of sulfur atoms [see Fig. 6(a)].\(^{37}\) Other phases consist of BS$_4$ tetrahedra, suggesting that the formation of sp$^3$-hybridized tetrahedral boron atoms is favorable under high-pressure.

$\text{B}_2\text{S}_3$ (H.P.) has a topologically interesting crystal structure composed of “macro-tetrahedra”. As shown in Fig. 6(b), the structure consists of two kinds of electrostatically neutral macro-tetrahedra, $[\text{B}_{18}\text{S}_{27}]^{0\pm}$ and $[\text{B}_{32}\text{S}_{48}]^{0\pm}$, built up from covalent BS$_4$-tetrahedra. These macro-tetrahedra connect each other by sharing BS$_4$-tetrahedra at the corners to form an interpenetrating “macro-zincblende-type” structure.\(^{38}\)

Two new high-pressure forms of $\text{CaB}_2\text{S}_4$ (I and II) were synthesized under 4–6.2 GPa. $\text{CaB}_2\text{S}_4$-I was formed at 4 GPa and 1000°C, while $\text{CaB}_2\text{S}_4$-II was formed at 6.2 GPa and 800–1100°C. Figures 6(c) and 6(d) depict the crystal structures of $\text{CaB}_2\text{S}_4$-I and II. $\text{CaB}_2\text{S}_4$-I crystallizes into a tetragonal structure containing isolated macro-tetrahedral unit represented by formulas of $[\text{B}_{10}\text{S}_{20}]^{10-}$. While, $\text{CaB}_2\text{S}_4$-II is isosstructural with a high-pressure polymorph of $\text{CaB}_2\text{O}_4$-IV,\(^{41}\) consisting of three-dimensional linkage of BS$_4$-tetrahedra with calcium atoms at the center of the S$_{12}$-icosahedra.\(^{39}\)

Eu$^{2+}$-doped $\text{CaB}_2\text{S}_4$ (I and II) was synthesized in the same way and their luminescent properties were examined. Both $\text{CaB}_2\text{S}_4$-I and II showed strong green emission but the excitation and emission spectra showed a different manner reflecting the difference in coordination environment of Eu$^{2+}$. The excitation spectrum of $\text{CaB}_2\text{S}_4$-I possessed a broad band ranging 340–460 nm, suggesting a possible application for LED lamps (Fig. 7).

![Fig. 5. Curie temperature of Mn-intermetallic compounds with closely related MnGe$_4$-type and Cu$_2$Sb-type structures.](image)

![Fig. 6. Crystal structures of some boron sulfides and ternary thioborates synthesized under high-pressure.](image)
2.4 Atom insertion into the “void”

High-pressure synthesis is also effective in “modifying” the void or cage of a specific crystal structure to create a functionality. This type of “material design” was demonstrated in the skutterudite-type thermoelectric materials to realize the concept of a “phonon-glass and electron-crystal”.[42]-[45]

Figure 8(a) shows the skutterudite-type structure often found in transition metal pnictides, TX₃ (prototype of mineral skutterudite is CoAs₃). The structure is composed of eight corner-shared TX₆ octahedra and the linked octahedra produce a void (cage) at the center of (TX₆)₈ cluster. This void is large enough to accommodate large metal atom (M), resulting in the formation of “filled-skutterudite” structures with the general formula MT₄X₁₂.

Generally the skutterudites are compounds of Group-9 transition elements (Co, Rh, Ir), while the filled-skutterudites are compounds of Group-8 transition elements (Fe, Ru, Os). This difference is due to the fact that the Group-8 skutterudite frameworks are “electron deficient” and the accommodation of metal atoms (void filling) is required to compensate the electron deficiency.

Filled skutterudites exhibit properties that comply with the concept of a “phonon-glass electron-crystal (PGEC)”, as proposed by Slack.[46] The metal atoms (fillers) act as “rattlers” because these atoms exhibit large thermal vibration amplitudes due to their weak bonding character to the frameworks. It is desirable that these loosely bound atoms give rise to strong phonon scattering without greatly affecting the essential part of the band structure of the skutterudites. The optimal filled skutterudite would have filler atoms loosely bonded to the skutterudite host lattice, although it is very difficult to satisfy this situation. Most attempts have employed by charge compensation of the host lattice to achieve high filling fractions above 50%. However charge compensation greatly affects the electronic structure, consequently the transport properties of the host materials. Another driving force, instead of charge compensation, is required to achieve the ideal void filling to realize the concept of PGEC.

By using high-pressure synthesis technique, CoSb₃-based skutterudites filled with Group-14 elements (Ge and Sn) were successfully synthesized with up to 100% filling fraction without charge compensation of the host lattice.[42]-[45] The structural analysis of the Sn-filled CoSb₃ (Sn₉Co₄Sb₁₂) revealed that the Sn atoms exhibit very large thermal vibration amplitude, indicative of a large “rattling” motion.[43] The Ge-filled and Sn-filled CoSb₃ exhibit drastic decrease in thermal conductivity as compared to normal CoSb₃ [Fig. 8(b)],[44],[45] while the favorable semiconducting nature of CoSb₃ is not substantially changed by Sn-filling. This result paved the way for further development of skutterudite-type thermoelectric materials using high-pressure synthesis technique.[47]-[50]

3. Microwave processing

Microwave (MW) processing of materials is one of the methods using “self-generation of heat”. If a material couples with MW electromagnetic wave energy, the material...
itself can be heated to high-temperature via material-MW interactions. In MW processing, the alternating electric field (E-field) and magnetic field (H-field) interact with the material during MW irradiation. The interactions are identified as energy losses in the materials, consisting of electric losses (conduction, dipole reorientation, space charging, and ionic polarization) and magnetic losses (hysteresis and eddy current). These energy losses cause a volumetric heating within the materials.\(^ {51} \) Microwaves can heat a material rapidly to a desired temperature since they transfer their energy to the material directly without thermal conduction process. It is also possible to quench the MW-processed material by simply switching off the MW power.

The resultant heat can be used to promote a chemical reaction with other components. Various ceramic processing such as powder synthesis, sintering, and joining are performed under MW irradiation and we can find many advantages of MW processing, especially short processing time as a result of enhancement of diffusion rate. These advantages are believed to be due to MW “thermal effects” and “non-thermal effects”,\(^ {52} \) those leading to possible non-equilibrium nature of MW-processed materials. We started the research on materials processing and chemical reactions controlled by MW energy (using 2.45 and 28 GHz frequency), aiming to clarify the existence of a microscopic thermally non-equilibrium state. During our extensive study, it has been revealed that “selective heating” of a specific component of reaction systems plays a key role on the formation of non-equilibrium structure.

In a selective heating system, we can expect different reaction mechanism under MW irradiation as compared to that under conventional heating. MW processing is essentially “non-equilibrium reaction” because the MW-material interacting behavior strongly depends on the nature of a material. For example, if a specific component in a chemical reaction system strongly couples with MW energy and the other component does not, solid-state diffusion mechanism of each species under MW electromagnetic field would much differ from that under conventional heating. In such a case, we can expect “one-way diffusion” in a microscopic scale.\(^ {53}, ^ {54} \)

### 3.1 Rapid formation and decomposition of supersaturated solid solution

The binary TiO\(_2\)–SnO\(_2\) phase diagram is well known to exhibit a miscibility gap at low temperature, possessing the spinodal decomposition in the temperature range 800–1400°C.\(^ {55} \) This binary system is a typical selective heating system under MW irradiation because SnO\(_2\) strongly couples with MW energy, whereas TiO\(_2\) does not.

MW irradiation to the equi-molar powder mixture of TiO\(_2\) and SnO\(_2\) was carried out using multi-mode MW heating system operated at 28 GHz frequency.\(^ {56} \) After a several minutes of MW irradiation, we got a fine modulated composite grains composed of Sn-rich and Ti-rich region (Fig. 9). In the transmission electron microscope (TEM) photograph, the bright part consists of Ti-rich phase and the dark part consists of Sn-rich phase. According to the binary phase diagram, lower temperature limit of the rutile-type solid solution region is 1400°C at the composition TiO\(_2\)–SnO\(_2\) = 1:1, and the composition exhibits phase separation below 1400°C.\(^ {55} \) In this case, however, formation of solid solution was completed at 1100°C in a short period under MW irradiation. The results suggest the following mechanism of the formation of the spinodal structure. At the initial stage of MW irradiation, SnO\(_2\) is selectively heated to a higher temperature and react with “cold” TiO\(_2\) species to form a supersaturated Ti\(_{1-x}\)Sn\(_x\)O\(_2\) solid solution via one-way diffusion. Anisothermal condition is maintained in a certain period and the temperature fluctuation within a microscopic scale induces the spinodal decomposition, consequently, the formation of microscopic lamellar structure.

Similar technique was applied to the binary ZnO–FeO\(_3\) system to obtain a nano-modulated semiconductor/magnetic material system. Recently, much attention has been paid for transition metal-doped ZnO as a DMS for its possible application to spintronics device. Experimentally, material design using non-equilibrium processing like pulsed laser deposition (PLD) and molecular beam epitaxy (MBE) is performed to make a superlattice structure of ZnO-based system.\(^ {57} \)

Using MW irradiation technique, nano-scaled modulated texture of ZnO/FeO\(_3\) (Zn:Fe = 1:1) system was successfully obtained as shown in Fig. 10(a). The formation of such a periodic modulated structure is an indication of the occurrence of spinodal decomposition. Figure 10(b) also shows the detailed analysis using line profile elemental analysis of the modulated structure along the line shown in Fig. 10(a). Here we can see the distinct phase separation that the bright phase contains 70 to 80% Fe (20–30% Zn) species and the dark phase contains 10 to 20% Fe (80–90% Zn) species. The periodicity of this modulated structure is about 40 nm. In addition, we also observed a formation of natural superlattice structure of Fe\(_2\)O\(_3\)(ZnO)\(_n\) homologous compounds.\(^ {58} \) Important fact is that these materials were synthesized by a simple procedure, only MW irradiation to the powder mixture of ZnO.
and \( \gamma'-Fe_2O_3 \), suggesting the following mechanism of the reaction. When MWs are irradiated to the powder mixture, rapid heating is achieved by strong coupling with MW energy. This gives a rapid formation of supersaturated solid solution with the wurtzite-type structure. This supersaturated solid solution is thermodynamically unstable and subsequent phase separation, spinodal decomposition, occurs during cooling step.

It is concluded that the non-equilibrium nature of MW selective heating, as well as rapid heating and quenching effects, plays a key role to form the nano-sized modulated texture. Generally most of DMSs are fabricated by artificial non-equilibrium techniques like MBE and PLD, MW processing will open a new field in surveying this type of materials.

### 3.2 Formation of new phase

The existence of stereo-active lone pair (5s\(^2\)) is an issue of concern of divalent tin (Sn\(^{2+}\)) compounds in view point of crystal chemistry of non-symmetric compounds and their functionality such as occurrence of ferroelectricity. Although Sn\(^{2+}\) compounds are thought to be candidates to replace the analogous Pb\(^{2+}\) compounds like ferroelectric Pb(Zr, Ti)O\(_3\) (PZT), it is difficult to synthesize complex oxides containing Sn\(^{2+}\) via solid-state reaction route. This is due to the fact that tin monoxide (SnO) tends to decompose to Sn metal and SnO\(_2\) (disproportionation reaction of Sn\(^{2+}\) to Sn\(^0\) and Sn\(^{4+}\)) above 300°C.\(^{59}\)

We have found a new synthetic strategy for a direct solid-state reaction to obtain Sn\(^{2+}\) compound, Sn\(_2\)TiO\(_4\), using a thermally non-equilibrium reaction field induced by MW selective heating.\(^{60}\) Binary SnO–TiO\(_2\) system exhibits a selective heating behavior under MW irradiation because SnO strongly absorbs MWs but TiO\(_2\) is nearly transparent to MWs. Under this situation, the reaction between SnO and TiO\(_2\) proceeds by the MW energy absorbed by SnO at the early stage of the reaction. By applying a simple MW heating technique to the powder mixture of SnO and TiO\(_2\), a new Sn\(^{2+}\) compound, Sn\(_2\)TiO\(_4\), could be successfully synthesized within a short period. The reaction possibly proceeds with the rapid diffusion of hot Sn\(^{2+}\) species toward TiO\(_2\) to form Sn\(_2\)TiO\(_4\). A drastic enhancement of reaction kinetics could be achieved under thermally non-equilibrium condition and this makes it possible to synthesize Sn\(^{2+}\) compounds, avoiding the disproportionation reaction of SnO. The compound, Sn\(_2\)TiO\(_4\), could not be synthesized by solid state reaction under conventional heating using an electric furnace or other external heating process using infrared rapid heating system.\(^{61}\) The results strongly suggest that MW processing is effective in synthesizing Sn\(^{2+}\) compounds by solid-state reaction using SnO as a starting material. From this point, a survey of new Sn\(^{2+}\) compounds by MW processing would become an attractive field in the near future.

### 3.3 Change in magnetic structure of spinel-type ferrites

Another example of “MW non-equilibrium phenomena” can be found in spinel-type ferrites. Among many ferrites with the spinel-type structure, zinc ferrite (ZnFe\(_2\)O\(_4\)) is known to crystallize into the cubic normal spinel-type structure where divalent cation (Zn\(^{2+}\)) occupies the tetrahedral sites and Fe\(^{3+}\) occupies the octahedral sites. ZnFe\(_2\)O\(_4\) is antiferromagnetic with the Neel temperature of 10 K. It was however revealed that MW-processed ZnFe\(_2\)O\(_4\) crystallites became X-ray amorphous and exhibited ferromagnetic (or ferrimagnetic) behavior. This phenomenon was first discovered in the powder synthesis experiment under multimode 28 GHz MW irradiation.\(^{62}\) In this experiment, powder mixture of ZnO and \( \alpha'-Fe_2O_3 \) was irradiated up to 1400°C at 2.0–4.0 kW MW power and the mixture turned glossy black after irradiation. Surprisingly, the product showed no diffraction peaks for X-ray and exhibited ferromagnetic behavior.\(^{62}\) Immediately after the first discovery, similar decrystallization behavior and the change in magnetic properties was also found in Fe\(_2\)O\(_3\) and BaFe\(_{12}\)O\(_{19}\) by Penn State group using a single-mode MW cavity operated at 2.45 GHz frequency.\(^{63,64}\) The single-mode experiments revealed that the MW magnetic field (H-field) plays an important role to form a non-equilibrium structure. Recent experiments on the synthesis of spinel-type FeAl\(_2\)O\(_4\) under MW H-field clearly indicated that the crystallite diameter of the irradiated speci-
men remarkably decreased as compared to that of conventionally heated one and the specimen has many nanodomain boundaries, those act as origin magnetic clusters. From these facts, it is considered that atom motion of magnetic ions under high frequency (28 GHz) MW field and/or 2.45 GHz MW H-field caused the structural change to form a magnetic cluster.

In conclusion, the observed ferro- or ferrimagnetic behavior of MW-processed ZnFe₂O₄ is not attributed to partial reduction of Fe³⁺ but possibly due to the formation of Fe³⁺(octahedral site)–O²⁻–Fe³⁺(tetrahedral site) magnetic cluster at nano-domain boundaries as illustrated in Fig. 12. It should be pointed out that similar change in magnetic properties was reported in high-pressure squeezed ZnFe₂O₄. In that case, formation of ferrimagnetic cluster was believed to be due to dislocation at (111) slip plane under strong shear stress. MW effects on the structure of magnetic materials should be further studied in terms of interaction between atom motion and MW electromagnetic wave.

4. Conclusion

As demonstrated in this article, chemical reaction under a specific external field is a promising route to discover new materials those open the way for breakthrough in future materials science. By applying high-pressure or microwave electromagnetic field to simple solid state reaction systems, one can discover non-equilibrium new materials those do not exist in the equilibrium phase diagram. Such challenges will break new ground in realizing materials design in the next decade of materials science and solid state chemistry. What we must emphasize is that there is still a lot of undiscovered new compounds with promising functionalities.

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