‘Soft solution processing’ *in situ* fabrication of morphology-controlled advanced ceramic materials in low temperature solutions without firing

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Abstract. A process called ‘soft solution processing’ has been introduced to fabricate advanced solid state materials in an economical, environmental friendly, and energy and material efficient way. A concise discussion of how to improve the synthetic conditions and how to extend the applied system is given. The successful examples show that soft solution processing is capable of preparing advanced materials with planned properties through the easy control of reaction conditions in a suitable aqueous solution in a single synthetic step without huge energy consumption for sintering or melting and without any sophisticated equipment.

Keywords. Soft solution processing; environmentally friendly processing; hydrothermal reaction; electrochemical reaction; electrochemical–hydrothermal reaction.

1. Introduction

Advances in the instrumentation and material have ameliorated modern human life and also caused us many environmental problems such as the wasted heat and material. Nevertheless, although an intensive attention is being paid mainly to the fabrication of advanced material and equipment with more sophisticated and complicated functions, the economic, environmental, and energy factors of the fabrication processes have not been adequately considered. The earth is an almost closed system with limited biosphere, lithosphere, hydrosphere and atmosphere (figure 1) (Murota 1983). Thus, the used materials would be recycled, moreover wasted energy and heat should be minimized. In addition, it should be noted that the process for the material recycling also requires energy consumption. Since the moderns cannot stop using advanced materials, an alternative synthetic route to the fabrication of advanced materials in an economical, less energy and material consuming, and environmentally friendly way should be obtainable. I believe that, in the near future, the research in the material science field can be only punctuated by such an alternative.

Before the mention of another important aspect in the material science field, the difference in the conception between ‘substance’ and the above-mentioned ‘material’ should be precisely defined. ‘Substance’ has a particular chemical composition, a certain physical state such as structure, and specified properties based on its composition and physical state. To define ‘material’, additional

factors such as shape and size should be accounted. In this regard, the fabrication of solid state ‘material’ may consist of the production of substance and the simultaneous or subsequent shape-forming. A number of prospective solid state substances have been produced with respect to their composition, structure, and properties. However, only a few of them can be considered to prepare useful materials, even though they have desired compositions, structures, and properties. It is ascribed that such solid state substances are extremely difficult to give desired shapes, forms, and sizes due to their high brittleness. This important point has often been overlooked.

Generally, the production of substance and the simultaneous or subsequent shape-forming can be performed by using solid, liquid, and/or gas phases. The conventional works to obtain solid state materials have been focused primarily on the usage of solid and molten state reaction at high temperature, i.e. ceramic processing. However, concerning compositional homogeneity, difficulty of shape-forming, and procedural energy consumption, the synthetic route using solid phase is not suitable. Otherwise, the synthetic route using molten or gas phases requires huge energy consumption. Despite various disadvantages such as high energy consumption and sophisticated instrumentation, the processing using gas phase and/or vacuum system such as CVD and sputtering has been extensively investigated lately. Each of these techniques are not economical nor environmental friendly. It will be discussed in detail later. In this manner, a glance at the diagram of phase transform concerned solid phase (figure 2) seems to give us a basic but important

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information to develop an alternative synthetic approach. In fact, the precipitation technique has often been involved to prepare desired substances in bulk. And, the detailed study of the interfacial corrosion has been done to protect the surface of metal. However, in the economic and environmental viewpoint, the fabrication of advanced and shaped inorganic material using such techniques has not been considered. In addition, the application of the simple precipitation or corrosion technique seems to be limited to the fabrication of few simple materials (Hirai 1997). Evidently, it is important to develop an economical, environmental friendly, single-step, and energy and material efficient process that can produce advanced and shaped inorganic materials. In the course of trying to develop such a novel synthetic approach, 'soft solution processing' seems to fit these criteria. In this contribution, we present the definition of 'soft solution processing', the basic nature of soft solution processing to be an economical, environmental friendly, and energy efficient process, some successful examples, as well as some possible synthetic improvement using designed soft solution processing methods.

2. Definition of soft solution processing

Soft solution processing is a term encompassing a wide group of synthetic processes used to prepare advanced solid state materials using a solution treatment at a low temperature. Here, 'soft' means less environmental charge, low energy consumption, no complicated instrumentation, and no sophisticated multistep processes. The solution treatment of the starting substances can be combined with different activation methods such as electrochemical reactions, photochemical excitation, hydrothermal reactions at low temperature, application of microwaves or ultrasonics, chimie douce reactions, bioactivation or hot-pressing to prepare desired materials. Since all living

organisms on earth consist of aqueous solution systems at ambient temperature and pressure, water should be the most suitable solvent for the soft solution processing. Therefore, spontaneous chemical reactions in aqueous solution such as precipitation or corrosion should be involved in the soft solution processing. In addition, due to the nature of the soft solution processing such as the facility in combining of the solution treatment with different activation methods, the applied systems in the fabrication of advanced materials can be extended.

3. Thermodynamic and environmental aspect of soft solution processing

We succeeded in fabricating some advanced ceramic materials using the soft solution processing in an economical, single-step, more environmental friendly, and less energy consuming way. It will be presented in the subsequent section. With respect to the properties of the obtained materials, it seems that there is no difference between soft solution processing and other synthetic routes using solid, molten, and/or gas phases. However, the difference in the total energy consumption between them is really striking. A much larger excess of energy is necessary to create molten, gas, vapour, or plasma phase than to form aqueous solution through dissolution at the same temperature (figure 3). Such concept can be easily elucidated using simple examples of NaCl and BaTiO₃ systems. In the case of NaCl, as shown schematically in figure 4 (Otaki 1995), its lattice energy (ΔG (lattice)) of 681 kJ/mol can be fully compensated by the Na⁺ and Cl⁻ hydration energies (ΔG (hydration)) of -727 kJ/mol. Therefore, the reactive and fluid species can be obtained by using spontaneous dissolution of NaCl without high energy consumption. That is more distinguishable in the case of BaTiO₃ system. The energy diagram for the formation of BaTiO₃ from various pre-

Figure 1. Entropy transfer in energy cycle on the earth (modified from Murota's (1983) figure).

Figure 2. Diagram of phase transform concerned solid phase.

cursors is shown in figure 5 (JANAF Thermochemical Tables, 1968–1982). Various reactions of BaTiO₃ formation can be described by the following equations:

The free energy changes (ΔG) for the given reactions (1), (2), and (3) are 38 kcal/mol, 727 kcal/mol, and 3685 kcal/mol, respectively, at room temperature. It means that any fabrication route using gas phase requires a huge activation energy to prepare advanced materials such as BaTiO₃. Moreover, such consumed energy would be discarded anyhow into our environment. In the environmental viewpoint, it is evident that solution processing is most environmental friendly, since solution processing is located in the pressure–temperature range characteristic for life cycling conditions on earth. As shown in the pressure–temperature diagram for various synthetic techniques for advanced ceramic materials (figure 6), the farther a certain processing is located from solution processing criterion, the more the environment stress is increased.

4. Successful application of soft solution processing

There are so many advanced inorganic materials with respect to their chemical composition, shape, and function. Since we are not able to study and discuss all of them, we should choose a certain substance and shape. In the course of choosing a suitable system, we should keep in mind some important aspects. At first, one of the most required techniques is a miniaturization of advanced inorganic materials such as microelectronics and micro-battery. It means that technical improvements in the fabrication of functional thin film are important. And, the major advanced ceramic materials contain at least one metal element with its particular oxidation state, coordination, and chemical composition. It is attributed to the specialized electronic configuration of the given metal species. As mentioned in the previous section, the best solvent for the soft solution processing is water. Here, it should be noted that the dissolved metal in aqueous solution are generally combined with oxygen derivatives such as hydroxyl group to form a certain anion such as metalite or metalate (Pourbaix 1974). In addition, such a anion containing metal can react on a cation present in the aqueous solution. In this way, why we may not obtain desired advanced ceramic material

films, when suitable dissolved metal species and cation can be provided and we can control their supersaturation position? It is well known that heterogeneous nucleation is much easier than homogeneous nucleation under the common conditions. It means that the formation of multicomponent oxide films is much easier than the coprecipitation of multicomponent oxide in bulk. Inductively, when a substrate desirably shaped and coated with suitable metal or alloy will be subjected to an aqueous solution in the sufficient presence of suitable cation, the film formation of multicomponent inorganic materials can be achieved. Based upon the above-presented information, the formation of some functional multicomponent oxide films using the soft solution processing has been accomplished in our laboratory. To list it concretely, we succeeded in fabricating the film of LiMO₂ (M = Co, Ni) (Han *et al* 1998a, b, c; Yoshimura *et al* 1998a), ABO₄ (A = Ca, Sr, Ba and B = W, Mo) (Cho and Yoshimura 1995a, b, 1997a, b; Cho *et al* 1995; Krttil and Yoshimura 1998) and their solid solution system (Cho and Yoshimura 1996b, 1997c; Cho *et al* 1996; Yoshimura *et al* 1997a, b), ATiO₃ (A = Ca, Sr, Ba) (Kajiyoshi *et al* 1994, 1996a, 1997; Yoshimura *et al* 1995; Suchanek *et al* 1998) and their solid solution system (Kajiyoshi *et al* 1996b; Yoshimura *et al* 1998b, c), BaFeO_{4-x} (Yoshimura 1992), LiNbO₃ (Yoshimura 1992), PbTiO₃ (Cho and Yoshimura 1997d) using soft solution processing methods. In addition, it is found that the planned properties of these films such as film thickness, surface morphology, and even chemical composition can be achieved through the active control of synthetic conditions.

4.1 LiMO₂ (M = Co and Ni) film electrodes for lithium rechargeable microbattery

Well crystallized and electrochemically active LiNiO₂ and LiCoO₂ film electrodes for lithium rechargeable microbatteries are fabricated in a single synthetic step using soft solution processing in a concentrated LiOH solution at fixed temperatures between 20 and 200°C without any post-synthesis heat treatment (Han *et al* 1998a, b, c; Yoshimura *et al* 1998a). The used LiOH solution containing dissolved nickel or cobalt species can be recycled by filtering it and replenishing the LiOH, which is environmentally and economically beneficial. While the purely hydrothermal treatment of cobalt metal plates directly leads to the formation of LiCoO₂ films, Ni(OH)₂ films on the surface of nickel metal plates are fabricated with the same hydrothermal conditions. By the use of the electrochemical–hydrothermal approach under supplementary galvanostatic charge with the same hydrothermal conditions, LiNiO₂ films can only effectively be prepared in a single synthetic step out of nickel metal plates (Han *et al* 1998a). Such difference in

designed combination of activation methods can be ascribed to the different metal cation valency between dissolved nickel species (that contain divalent nickels) and dissolved cobalt species (that should possess trivalent cobalts). The prepared films exhibit a prospective electrochemical activity, however, the film property is dependent on the synthetic conditions. In the fabrication of LiCoO_2 films in particular, a reasonable electrochemical activity was observed for the whole films prepared between 20 and 200°C. However, while spinel (space group $Fd3m$) lithium cobalt oxide films were prepared under 100°C, mainly layered (space group $R\bar{3}m$) LiCoO_2 films were prepared over 100°C (Han *et al* 1998a, c). The effect of synthetic conditions in the Ni system is different from that in the Co system. A reasonable electrochemical activity was observed for the films prepared at fixed temperatures between 125 and 170°C (Han *et al* 1998b). Such differences in the fabrication methods and the properties of the prepared films indicate the importance of the synthetic conditions and their influence on the reaction mechanism. According to the film formation mechanism study, the reaction pathway of LiNiO_2 film formation can be described by the following equations (Han *et al* 1998b):

Otherwise, the reaction pathway of LiCoO_2 film formation can be given as follows (Han *et al* 1998a):

The film formation mechanism study elucidates the synthetic condition effect and also shows that soft solution processing is capable of preparing advanced inorganic materials with planned properties through the active control of reaction conditions.

4.2 Luminescent films of ABO_4 ($A = \text{Ca, Sr, Ba}$ and $B = \text{W, Mo}$) and their solid solution system

AWO_4 , AMoO_4 ($A = \text{Ca, Sr, Ba}$), and their solid solution system with a scheelite structure have been used in various fields such as electro-optics and microwave materials, since the AWO_4 and AMoO_4 may produce

blue and green luminescence, respectively (Kröger 1948; Johnson *et al* 1962; Porto and Scott 1967; Blasse and Schipper 1974; Grasser *et al* 1988; Paski and Blades 1988). For the advanced application, the fabrication of their films is so important that various techniques including CVD, sputtering, and sol-gel deposition have been adopted. However, the films prepared by such techniques show no luminescence due to their poor crystallinity (Feldman 1958; Kashiwakura and Kanehisa 1989). Since soft solution processing presents several advantages such as the facility of control on the film thickness and surface morphology, the formation of the above-mentioned films has been attempted using soft solution processing. The successful fabrication was achieved by the electrochemical treatments of W or Mo metal plates in the solution of Ca(OH)_2 , Sr(OH)_2 , and/or Ba(OH)_2 at room temperature under galvanostatic (1.0 mA/cm²) or potentiostatic (0.1 V) condition. The analysis of electrochemical as well as electrochemical quartz crystal microbalance (EQCM) data taken during these experiments identifies at least three qualitatively different steps comprising of the electrode process (Krtić and Yoshimura 1998). In detail, in the case of BaWO_4 system, it can be described as a consequence of three steps:

As shown in table 1, their luminescence properties at different temperatures have been confirmed, which indicates their high crystallinity and purity (Cho *et al* 1995a, b, 1996a, b, c, 1997c; Yoshimura *et al* 1997a, b).

4.3 ATiO_3 ($A = \text{Ca, Sr, Ba}$) films, their solid solution system, and their compositionally graded films

ATiO_3 ($A = \text{Ca, Sr, Ba}$) and their solid solution system with a cubic perovskite structure have drawn a great interest due to their unusual dielectric properties with a small temperature coefficient and reduced leakage current, as well as electro-optic properties (Dimos 1995; Cross 1996). Additionally, since their films are promising candidates for new generation DRAM capacitors and photocatalysts, their film formation has been extensively investigated (Jones Jr *et al* 1995; Suzuki 1995). However, all the previous works to fabricate the films such as CVD, sputtering, and sol-gel deposition required post-synthesis heat treatments at high temperatures above 500°C to crystallize the pre-deposited amorphous film or to fire the organic precursor to yield an appropriate

composition (Sreenivas *et al* 1987; Xu and Mackenzie 1992; Yano *et al* 1994; Lee *et al* 1995; Wessels 1995). Such heat treatments often result in cracking and/or peeling of the obtained ATiO_3 films. In this way, well crystallized ATiO_3 ($A = \text{Ca}, \text{Sr}, \text{Ba}$) films, their solid solution system, and their compositionally graded films are fabricated using differently modified electrochemical-hydrothermal methods depending on the systems. The detailed synthetic conditions have been previously described (Kajiyoshi *et al* 1994, 1996a, b, 1997; Suchanek *et al* 1998; Yoshimura *et al* 1995, 1998b, c). Although the precise representation of the actual reaction mechanism for the film formation has still not been accomplished, possible reaction pathways can be proposed as shown in figure 7. With respect to the film properties, in the case of the fabricated BaTiO_3 film, the resistivity of $10^{12} \Omega\text{-cm}$ was obtained in the voltage range up to 2 V for the film $0.40 \mu\text{m}$ thick and its breakdown voltage was higher than 12 V. The grown films were paraelectric with dielectric constants of 340–350 and dielectric losses of 7–10% at 1 kHz, $0.1 V_{\text{rms}}$, and 25°C . The capacitance variation with dc bias voltage from -2.5 to $+2.5$ V was 9% of the zero-bias value, and that with temperature from -60°C to 130°C was 24% of the room temperature value (Kajiyoshi *et al* 1997).

5. Synthetic improvement using designed soft solution processing

The successful preparation of various functional multi-component oxide films in a single synthetic step using

Figure 3. Schematic energy diagram ($G-T$) in a single component system.

soft solution processing without any post-synthesis annealing has several important impacts on the synthetic approaches in the preparation of advanced ceramic materials. At first, it is the most economical and environmental friendly synthetic route. Compared with the processing using gas phase and/or vacuum system such as CVD and sputtering, such processing usually represents highly sophisticated multistep fabrication procedures including preparation of desired substance in bulk or its precursors, deposition or integration on substances, shaping and orientation, as well as post-synthesis heat treatments. What is worse, the structure and chemical composition of the pre-deposited substance, what we call a 'target', are not identical to those of the film prepared by the deposition techniques as well as the target itself after the deposition. In comparison with sol-gel coating techniques, we are not able to find cheaper organic solvent than water. And, serious film discontinuity often occurs upon sol-gel firing. Moreover, the sol-gel firing also causes air pollution. Now, the economic and environmental advantages of soft solution processing are clear to see. The facility in applying solution gives the

Figure 4. Born-Haber cycle of ionization and hydration of NaCl.

versatility in shaping, up-sizing, and orienting desired material films. And, the activation method can be easily modified, substituted, and/or combined with other activation methods in order to introduce more economical, energy and material efficient, and environmental friendly synthetic strategy, as well as to extend the applied systems in the fabrication of advanced materials. In addition, morphology and chemical composition of the prepared materials can be easily controlled by adjusting the synthetic conditions.

6. Conclusion

The fabrication of various functional multicomponent oxide films has been achieved using suitable soft solution processing methods. The films prepared by soft solution processing show the desired and prospective properties despite their low temperature synthesis and no post-synthesis annealing. The implementation of soft solution processing to make advanced materials shows a successful example of how to improve desired material preparation

Figure 5. Energy diagram for the formation of BaTiO_3 using solid and/or gas precursors (g, s and c correspond to the gas, solution, and crystal state, respectively). Compiled from the data in JANAF Thermochemical Tables.

Figure 6. Schematic pressure-temperature diagram for various synthetic techniques for advanced ceramic materials.

Table 1. Comparison of the emission and excitation wavelength values observed in the luminescence spectra of the ABO_4 (A = Ca, Sr, Ba and B = W, Mo) films prepared by using soft solution processing.

Compounds	Blue or green emission (temperature*)	Excitation (temperature*)
SrWO_4	461 nm (LNT)	248 nm (LNT)
SrMoO_4	536 nm (LNT)	285 nm (LNT)
CaWO_4	456 nm (RT) 465 nm (LNT)	254 nm (RT) 251 nm (LNT)
CaMoO_4	536 nm (LNT)	285 nm (LNT)
$\text{Sr}_{1-x}\text{Ba}_x\text{WO}_4$	461 ± 2 nm (LNT)	248 ± 2 nm (LNT)
$\text{Ba}_{1-x}\text{Sr}_x\text{MoO}_4$	536 ± 2 nm (LHT)	285 ± 2 nm (LHT)
$\text{Sr}_{1-x}\text{Ca}_x\text{WO}_4$	463 ± 2 nm (LNT)	250 ± 2 nm (LNT)
$\text{Sr}_{1-x}\text{Ca}_x\text{MoO}_4$	536 ± 2 nm (LNT)	285 ± 2 nm (LNT)
$\text{Ba}_{1-x-y}\text{Sr}_x\text{Ca}_y\text{WO}_4$	461 ± 2 nm (LNT)	248 ± 2 nm (LNT)

*RT: Room temperature

LNT: Liquid-nitrogen temperature

LHT: Liquid-helium temperature.

Figure 7. Possible reaction pathways for the $ATiO_3$ ($A = Ca, Sr, Ba$) film formation.

by design of experimental condition of the micro-structuring mechanism. Therefore, soft solution processing should be expected to serve as a new strategy for the fabrication of advanced ceramic materials.

References

- Blasse G and Schipper W J 1974 *Phys. Status Solidi* **A25** K163
- Cho W S and Yoshimura M 1996a *Jpn J. Appl. Phys.* **35** L1521
- Cho W S and Yoshimura M 1996b *Jpn J. Appl. Phys.* **35** L1449
- Cho W S and Yoshimura M 1997a *Jpn J. Appl. Phys.* **36** L1216
- Cho W S and Yoshimura M 1997b *Solid State Ionics* **100** 143
- Cho W S and Yoshimura M 1997c *Jpn J. Appl. Phys.* **36** 5658
- Cho W S and Yoshimura M 1997d *J. Mater. Res.* **12** 833
- Cho W S, Yashima M, Kakihana M, Kudo A, Sakata T and Yoshimura M 1995a *J. Am. Ceram. Soc.* **78** 3110
- Cho W S, Yashima M, Kakihana M, Kudo A, Sakata T and Yoshimura M 1995b *Appl. Phys. Lett.* **66** 1027
- Cho W S, Yashima M, Kakihana M, Kudo A, Sakata T and Yoshimura M 1996c *Appl. Phys. Lett.* **68** 137
- Cross L E 1996 *Ceram. Trans.* **68** 15
- Dimos D 1995 *Annu. Rev. Mater. Sci.* **25** 273
- Feldman C 1958 *J. Soc. Motion Pict. Eng.* **67** 455
- Grasser R, Pompe W and Scharmann A 1988 *J. Lumin.* **40/41** 343
- Han K S, Song S W and Yoshimura M 1998a *Chem. Mater.* **10** 2183
- Han K S, Krti P and Yoshimura M 1998b *J. Mater. Chem.* **8** 2043
- Han K S, Song S W and Yoshimura M 1998c *J. Am. Ceram. Soc.* **81** 2465
- Hirai T 1997 *Proceedings of the FGM symposium* (Osaka, Japan) in Japanese
- JANAF Thermochemical Tables 1968–1982 National Bureau of Standards, American Chemical Society, American Institute of Physics
- Johnson L F, Boyd G D, Nassau K and Soden R R 1962 *Phys. Rev.* **126** 1406
- Jones Jr R E, Zurcher P, Chu P, Taylor D J, Lii Y T, Jiang B, Maniar P D and Gillespie S J 1995 *Microelectron. Eng.* **29** 3
- Kajiyoishi K, Tomono K, Hamaji Y, Kasanami T and Yoshimura M 1994 *J. Am. Ceram. Soc.* **77** 2889
- Kajiyoishi K, Hamaji Y, Tomono K, Kasanami T and Yoshimura M 1996a *J. Am. Ceram. Soc.* **79** 613
- Kajiyoishi K, Yoshimura M, Hamaji Y, Tomono K and Kasanami T 1996b *J. Mater. Res.* **11** 169
- Kajiyoishi K, Sakabe Y and Yoshimura M 1997 *Jpn. J. Appl. Phys.* **36** 1209
- Kashiwakura Y and Kanehisa O 1989 Japan Patent No. 1-263188
- Kröger F A 1948 *Some aspects of the luminescence of solids* (Amsterdam: Elsevier) p. 107
- Krti P and Yoshimura M 1998 *J. Solid State Electrochem.* (in press)
- Lee M B, Kawasaki M, Yoshimoto M and Koinuma H 1995 *Appl. Phys. Lett.* **66** 1331
- Murota T 1983 *Economy of entropy and energy* (Tokyo: Tokyo Keizai Shinposha Ltd.) in Japanese
- Otaki H 1995 *Hydration of ions* (Tokyo: Kyoritsu Shuppan Publ. Ltd.) in Japanese
- Paski E F and Blades M W 1988 *Anal. Chem.* **60** 1224
- Porto S P S and Scott J F 1967 *Phys. Rev.* **157** 716
- Pourbaix M 1974 *Atlas of electrochemical equilibria in aqueous solutions* (Houston, Texas: National Association of Corrosion Engineers) Second Ed.
- Sreenivas K, Mansingh A and Sayer M 1987 *J. Appl. Phys.* **62** 4475
- Suchanek W, Watanabe T and Yoshimura M 1998 *Solid State Ionics* **109** 65
- Suzuki M 1995 *J. Ceram. Soc. Jpn.* **103** 1099
- Wessels B W 1995 *Annu. Rev. Mater. Sci.* **25** 525
- Xu Y and Mackenzie J D 1992 *Integrated Ferroelectrics* **1** 17
- Yano Y, Iijima K, Daitoh Y, Terashima T, Bando Y, Watanabe Y, Kasatani H and Terauchi H 1994 *J. Appl. Phys.* **76** 7833
- Yoshimura M 1992 *Proc. Symp. Mater. Res. Soc.* **271** 457
- Yoshimura M, Urushihara W, Yashima M and Kakihana M 1995 *Intermetallics* **3** 125
- Yoshimura M, Ohmura M, Cho W S, Yashima M and Kakihana M 1997a *J. Am. Ceram. Soc.* **80** 2464
- Yoshimura M, Ohmura M, Cho W S, Yashima M and Kakihana M 1997b *Jpn. J. Appl. Phys.* **36** L1229
- Yoshimura M, Han K S and Tsurimoto S 1998a *Solid State Ionics* **106** 39
- Yoshimura M, Asai O, Cho W S, Yashima M, Suzuki Y and Kakihana M 1998b *J. Alloys & Compounds* **265** 132
- Yoshimura M, Suchanek W, Watanabe T, Sakurai B and Abe M 1998c *J. Mater. Res.* **13** 875