

Soft Solution Processing : Low-Energy Direct Fabrication of Advanced Inorganic Materials

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A new concept "soft solution processing" has been introduced to fabricate advanced solid state materials in an economical, environmentally friendly, and energy and material efficient way. The prepared films show the desired and prospective properties despite of low temperature synthesis and no post-synthesis annealing. Successful examples demonstrate 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 and without any sophisticated equipment.

Introduction

As advances in the instrumentation and material have ameliorated modern human life, the demand to develop more sophisticated and complicated functions increases. Especially, one of the most required techniques is a miniaturization of advanced inorganic materials such as microelectronics. It means that technical improvements in the fabrication of functional thin films are important. However, although an intensive attention is being paid mainly to the fabrication of more delicate and advanced material, the economic, environmental, and energy factors of the fabrication processes have not been adequately considered. Since the earth is an almost closed system, the used materials would be recycled, moreover wasted energy and heat should be minimized. Thus, if the production of desired substance, the simultaneous shape-forming and in situ compositional and functional grading can be performed in only one synthetic step at low temperature with high energy and material efficiency, it should be the most effective synthetic route. Unfortunately, the usual synthetic approaches described in previous works to fabricate thin films have been mainly focused on multistep processes using gas phase and/or vacuum system. These processes include the following: preparation of a bulk material or its precursors; deposition or integration onto/into substrates using chemical vapor deposition, sputtering, or laser ablation deposition; the formation of shape; size; and orientation. In addition, post-synthesis heat treatments are often required to allow proper functions. Since huge energy consumption and sophisticated instrumentation are required in these methods, these techniques are not economical nor environmentally friendly. In the course of trying to developing such a novel synthetic

approach, "soft solution processing" seems to fit these criteria. In this contribution, we explain what is soft solution processing and how soft solution processing can be realized to obtain advanced inorganic materials. In addition, several successful examples and some possible synthetic improvement using designed soft solution processing methods will be given.

Definition and Nature 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 and material consumption, no complicated instrumentation, and no sophisticated multistep processes. The solution treatment of the starting substances can be easily combined with different activation methods such as electrochemical reactions, photochemical excitation, hydrothermal reactions at a 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 dissolution, precipitation and/or interfacial reaction should be involved in the soft solution processing. In addition, 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. 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.¹ Such an anion containing metal can react on a cation present in the aqueous solution. In this way, why we may

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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. Thus, 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.

Successful Application of Soft Solution Processing

Soft solution processing has been used to fabricate several morphology-controlled advanced ceramic materials in an economical, environmentally friendly, and energy and material efficient way. For example, we succeeded in fabricating the $\text{Li}_{1-x}\text{Ni}_{1+x}\text{O}_2$ and LiCoO_2 films for Li rechargeable microbattery,²⁻⁵ luminescent films of ABO_4 ($A = \text{Ca, Sr, Ba}$ and $B = \text{W, Mo}$) and their solid solution system,⁶⁻¹² and ATiO_3 ($A = \text{Ca, Sr, Ba}$) films and their solid solution system for new generation DRAM capacitors.¹³⁻¹⁷

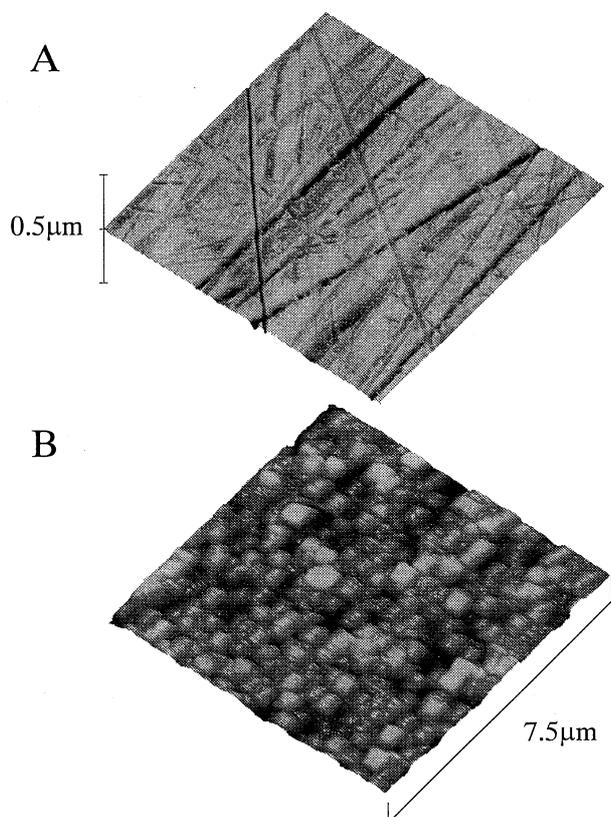


Figure 1. Atomic force microscopy images of (A) Ni metal substrate and (B) $\text{Li}_{1-x}\text{Ni}_{1+x}\text{O}_2$ film fabricated at 125 °C with 1.0 mA/cm².

$\text{Li}_{1-x}\text{Ni}_{1+x}\text{O}_2$ and LiCoO_2 films are fabricated in a single synthetic step in a concentrated LiOH solution at fixed temperatures between 20 and 200 °C without any post-synthesis heat treatment.²⁻⁵ Figure 1 directly demonstrates the evolution of the surface morphology during the soft solution processing. While the purely hydrothermal treatment of cobalt metal plates directly leads to the formation of LiCoO_2 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, $\text{Li}_{1-x}\text{Ni}_{1+x}\text{O}_2$ films can only effectively be prepared in a single synthetic step out of nickel metal plates.³ 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). In the case of Ni system, the films prepared between 125 and 175 °C exhibit a prospective electrochemical activity.⁴ In the case of Co system, a reasonable electrochemical activity was observed for the whole films prepared between 20 and 200 °C. However, while spinel (space group $\text{Fd}\bar{3}\text{m}$) lithium cobalt oxide films were prepared below 100 °C, mainly layered (space group $\text{R}\bar{3}\text{m}$) LiCoO_2 films were prepared over 100 °C.^{3,5}

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.^{18,19} The successful film fabrication of AWO_4 , AMoO_4 ($A = \text{Ca, Sr, Ba}$) films, and their solid solution system 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. As shown in Figure 2 and Table 1, their luminescence properties have been confirmed, which indicates their high crystallinity and purity.^{7,9-12}

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

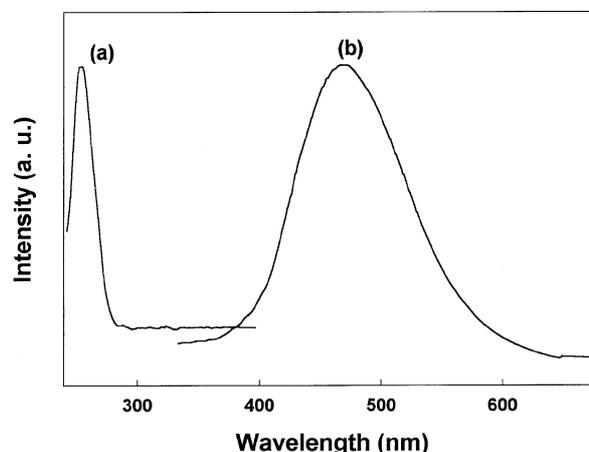


Figure 2. (A) Excitation and (B) emission spectra of the prepared SrWO_4 film at liquid nitrogen temperature (−196 °C).

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)	254 nm (RT)
	465 nm (LNT)	251 nm (LNT)
$CaMoO_4$	536 nm (LNT)	285 nm (LNT)
$Sr_{1-x}Ba_xWO_4$	461 ± 2 nm (LNT)	248 ± 2 nm (LNT)
$Ba_{1-x}Sr_xMoO_4$	536 ± 2 nm (LHT)	285 ± 2 nm (LHT)
$Sr_{1-x}Ca_xWO_4$	463 ± 2 nm (LNT)	250 ± 2 nm (LNT)
$Sr_{1-x}Ca_xMoO_4$	536 ± 2 nm (LNT)	285 ± 2 nm (LNT)
$Ba_{1-x}Sr_xCa_yWO_4$	461 ± 2 nm (LNT)	248 ± 2 nm (LNT)

*RT: Room temperature. LNT: Liquid-nitrogen temperature. LHT: Liquid-helium temperature

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.²⁰ Additionally, since their films are promising candidates for new generation DRAM capacitors and photo-catalysts, their film formation has been intensively investigated.²¹ Well crystallized $ATiO_3$ ($A = Ca, Sr, Ba$) films and their solid solution system are fabricated using differently modified electrochemical-hydrothermal methods depending on the systems. The detailed synthetic conditions have been previously described.¹³⁻¹⁷ With respect to the film properties, in the case of the fabricated $BaTiO_3$ film, the resistivity of $10^{12} \Omega \cdot cm$ was obtained in the voltage range up to 2 V for the film $0.40 \mu m$ 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, $0.1 V_{rms}$, and $25^\circ C$. 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 $-60^\circ C$ to $130^\circ C$ was 24% of the room temperature value.¹³

In addition, the compositionally graded films of the above-

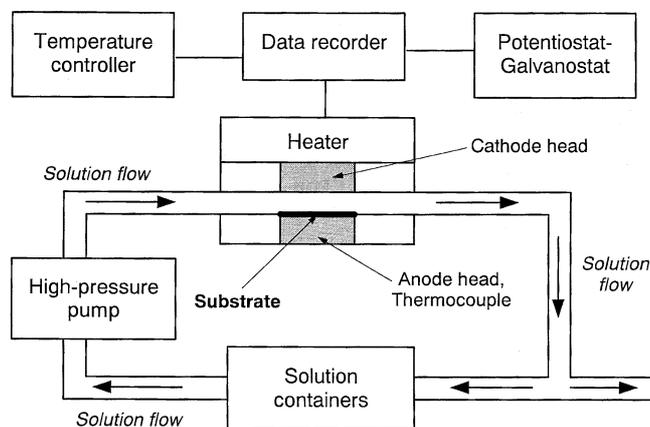


Figure 3. General schema of the laboratory-made reaction vessel for the fabrication of compositionally graded films.

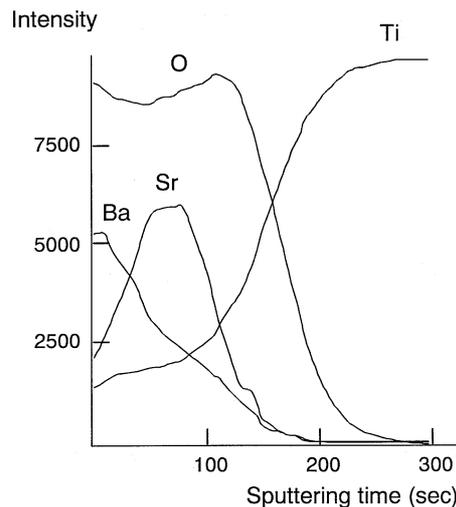


Figure 4. X-ray photoelectron spectroscopy depth profiles of Sr(3d), Ba(3d), Ti(2p), and O(1s) for $BaTiO_3/SrTiO_3/Ti$ double layer film.

mentioned materials are also fabricated by the successive application of different solutions using a laboratory-made reaction vessel (Figure 3). Depth profiles of Figure 4 show the successful fabrication of compositionally and functionally graded multilayer films.¹⁷

Conclusion

The successful preparation of various functional multi-component oxide films in a single synthetic step using soft solution processing without any post-synthesis annealing has several important impacts on the synthetic approaches in the preparation of advanced ceramic materials. The facility in applying solution gives the 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 environmentally friendly synthetic route, 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. Therefore, soft solution processing should be expected to serve as a new strategy for the fabrication of advanced ceramic materials.

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