Journal of Korean Association of Crystal Growth
Vol. 9, No. 5 (1999) 475-479

Synthesis and characterization of powders in the La-Al-Si-O system

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(Received June 9, 1999)

Abstract Langasite ($La_3Ga_5SiO_{14}$) was found to have wide application as a promising piezoelectric material. It has high thermal stability of the frequency and large electromechanical coupling factor. For the further development of new compounds with langasite type structure, powders in the La-Al-Si-O system were synthesized by a modified Pechini process. The evolution of the crystalline phase during calcination was studied using TG-DTA, XRD and TEM for the precursor powders. Decomposition proceeded via dehydration and removal of excess solvents at low temperatures ($T < 500°C$), followed by the crystallization of lanthanum aluminum silicate ($T > 800°C$) and phase transformation to $LaAlO_3$ phase ($T > 1200°C$). Transmission electron microscopy (TEM) of the calcined powders showed diffuse hollow rings corresponding to an amorphous phase at 800°C and clear diffraction patterns corresponding to a crystalline phase from the P321 space group ($T < 1200°C$) and the R3m ($T > 1200°C$).

1. Introduction

$A_3B_xC_{6-x}O_{14}$ compounds with Ca-gallogermanate structure ($Ca_3Ga_2Ge_4O_{14}$, sp. gr. P321) are promising materials for quantum electronics and acoustic application [1]. $A_3B_xC_{6-x}O_{14}$ single crystals such as langasite ($La_3Ga_5SiO_{14}$: LGS) exhibit piezoelectric properties; the electromechanical properties of the materials studied are close to or better than those of the most widespread piezoelectric - quartz, the acoustic Q-factor being substantially higher than that of quartz [2, 3].

LGS is a promising piezoelectric material which exhibits intermediate properties of piezoelectricity between those of quartz and lithium tantalate [2, 3]. LGS crystal has been investigated for laser devices mainly in Russia since the 1980s [4]. It has been studied for the application of SAW, BAW and resonator devices, due to it's acoustic characteristics [5-7].

Recently, LGS and its various modified forms have been synthesized using solid-state reactions and their single crystals were grown by the typical Czochralski (Cz) growth method [2, 3, 8]. Some of these have been noted as a superior piezoelectric material, and have larger piezoelectric constants than that of LGS.

For the further development of new compounds with LGS type structure, we have adapted advanced chemical solution methods [10-13]. The polymerized complex method as a modified Pechini method [14], where several metal ions in a solution are first chelated to form metal complexes and then polymerized to form a gel, seems to be most suitable among such chemical solution processes because homogeneously dispersed but rigidly fixed cations in the polymer network would have less chance to segregate even during pyrolysis. It has already successfully prepared highly pure samples of various oxides such as $BaTiO_3$ [11, 15, 16], many perovskite-type oxide [12-14] and even for various superconductors with multiple cationic compositions.

In this work, we reported the results of studying the process of LGS type powder synthesis, crystallization process and effect of heat-treatment in the La-Al-Si-O system.

2. Experimental procedure

The process of raw material synthesis is shown in Fig. 1. Anhydrous citric acid, $HOC(CO_2H)(CH_2CO_2H)_2$ (98 %, Aldrich Chemical Co., Milwaukee, WI), was first dissolved into ethylene glycol, $HOCH_2CH_2OH$ (99.5 %, Wako Pure Chemical Industries, Ltd., Japan), with the mole ratio of citric acid to ethylene glycol 1 : 4, and then 0.01 mole of tetraethyl orthosilicate,

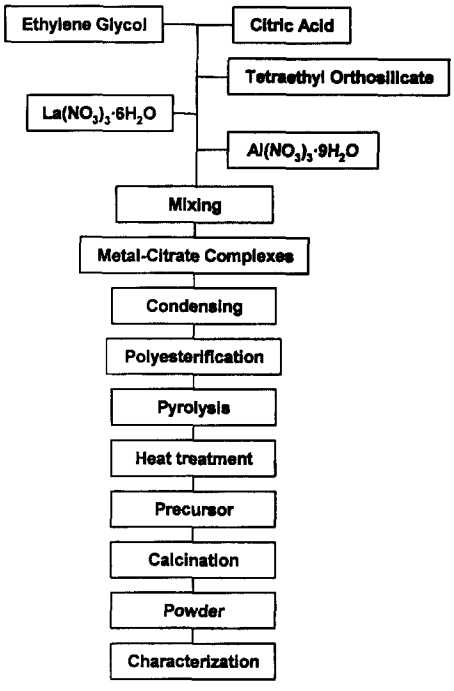

Fig. 1. Flowchart for powder preparation by the polymerized complex method.

$(C_2H_5O)_4Si$ (95 %, Wako Pure Chemical Industries, Ltd., Japan), was added into this solution. After achieving complete dissolution, 0.03 mol of lanthanum nitrate, $La(NO_3)_3 \cdot 6H_2O$ (99.9 %, Wako Pure Chemical Industries, Ltd., Japan), was dissolved followed by the addition of 0.05 mol of aluminum nitrate, $Al(NO_3)_3 \cdot 9H_2O$ (99.9 %, Aldrich Chemical Co., Milwaukee, WI). The mixture was stirred at 80°C for 2 h until it became transparent. The solution was heated at 150°C for several hours to promote the ester reaction between citric acid and ethylene glycol. As the solution became concentrated, it became highly viscous indicating the formation of a polymeric gel. Noteworthy is that neither precipitation nor turbidity has been formed during the polymerization. The viscous product was pyrolyzed at about 350°C to remove residual solvent and organics. After pyrolysis, black solid mass was obtained. Again this solid was heat-treated at 600°C for 5 h and used as a precursor. The precursor thus obtained was ground and calcined in air at 800~1300°C for 3 h.

The thermal behavior of precursor was characterized by thermogravimetric-differential thermal analysis (TG-DTA, Model 92-16.18, SETARAM, Caluire, France) with the precursor powder heated at a constant rate of 5°C/min in air up to 1400°C. Phase identification was carried out by the use of a standard powder X-ray diffractometer (XRD, D/Max-IIC, 40 kV, 30 mA, Rigaku Corporation, Tokyo, Japan) using CuKα radiation. The scan rate was 2°/min for the phase identification. Transmission electron microscopy (TEM) and Electron diffraction patterns (EDP) were observed using a JEOL JEM2010 (122 μA, 200 kV).

3. Results and discussions

Figure 2 shows typical TG-DTA curves of powder precursor heated in air. With an increase in temperature, the slight weight loss continues in the TG curve up to about 500°C. At above 500°C, the weight remains constant, indicating the decomposition of all organic components in the precursor. On the other hand, in the DTA curve, there are three exotherm peaks. The large exothermic peak to the left is due to the decomposition of organics. Sharp center peak at about 1000°C and the final peak at around 1300°C can be attributed to the onset of crystallization and phase transformation.

XRD patterns of the starting powder precursor and powder calcined in air at different temperatures for 3 h are shown in Fig. 3 in a 2θ range of 20~60°. The starting powder precursor and powder clacined at 800°C for 3 h were primarily amorphous in structure, as is characterized by the broad continuum (Fig. 3 (a), (b)). Drastic crystallization has occurred during the heat-treatment of the powder precursor in air at 900°C for 3 h. However, a lot of poorly defined peaks for the sample calcined at 900°C (Fig. 3 (c)) have evolved, which correspond to reflection from the intermediate phase. The XRD patterns of 1000°C and 1100°C (Fig. 3 (d), (e)) exhibited a characteristic peaks of LGS

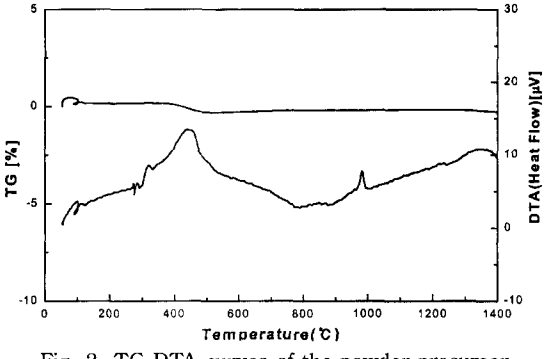

Fig. 2. TG-DTA curves of the powder precursor.

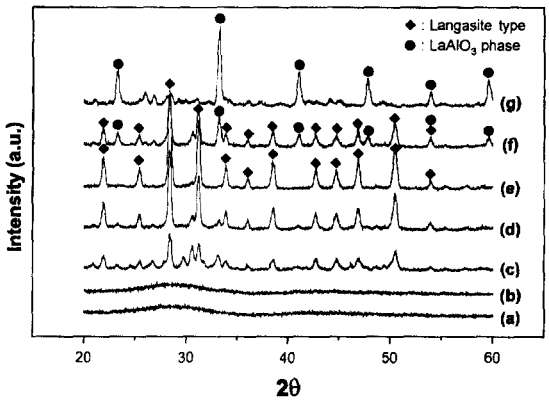

Fig. 3. XRD patterns of the precursor heat-treated at (a) 600°C for 5 h and powder calcined at (b) 800°C, (c) 900°C, (d) 1000°C, (e) 1100°C, (f) 1200°C, and (g) 1300°C for 3 h.

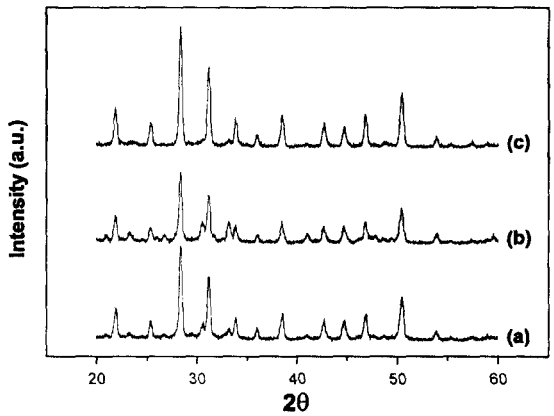

Fig. 4. XRD patterns of the powder calcined at 1000°C for (a) 3 h, (b) 12 h, and (c) 48 h.

family group materials. The peaks gradually sharpen with increasing firing temperature, which indicates an increase of crystallinity. Firing at temperatures above 1200°C (Fig. 3 (f)) brings about a phase transformation. This transformation should be accompanied by the ordering of the cation and anion sublattices during heating at temperatures higher than 1200°C, which results in the formation of $LaAlO_3$ phase (Fig. 3 (g)). This indicates that the $La_3Al_5SiO_{14}$ phase obtained in the present study is more likely to be of a stable phase below 1200°C. At above 1300°C, $LaAlO_3$ formed by phase separation during heat-treatment becomes

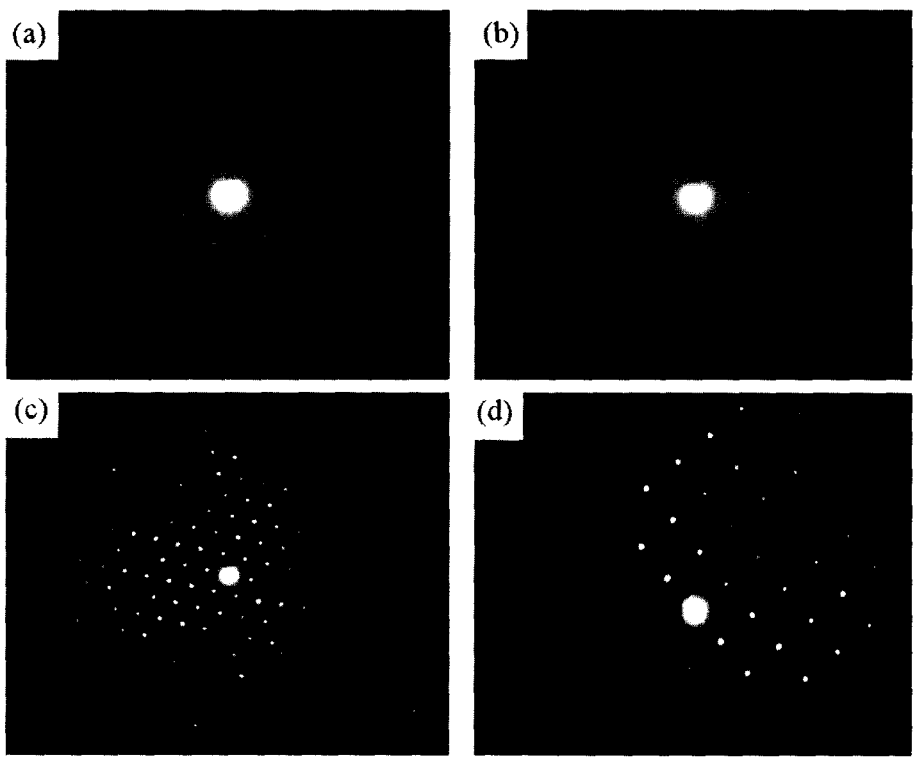

Fig. 5. Electron diffraction patterns of (a) powder precursor and powders calcined at (b) 800°C, (c) 900°C, and 1200°C for 3 h.

the main phase. Some of free SiO_2 and Al_2O_3 precipitate during heat-treatment at high temperatures, and the rest seem to coexist with the $LaAlO_3$ phase.

In the case of calcination time dependence, no phase transformation was observed. Equilibration in air at 1000°C for 48 h (Fig. 4) confirms the stability of this phase. We note that this phase could be formed and stabilized at temperatures below 1200°C.

The crystallization process has been also investigated using TEM. EDP analysis was performed for all samples prepared through calcination at different temperatures for 3 h. The evolution process of the crystallites from the precursor matrix seems to be rather clear. At below 800°C, the EDPs showed only diffuse hollow rings, corresponding to an amorphous phase (Fig. 5 (a)). At 800°C, the EDP shows that the amorphous phase still exists in the main parts of the matrix (Fig. 5 (b)). Some parts, particularly in the thin boundary range between particles, show crystalline phase. However, at above 800°C, clear polycrystal EDPs can be obtained, indicating no amorphous phases. With increasing temperature, at 900°C, clear diffraction pattern was observed indicating microcrystalline formation (Fig. 5 (c)). This means that the incipient crystallizing temperature could be as low as 900°C, corresponding to the previously mentioned XRD results. At above 1000°C, clear diffraction patterns were observed from the trigonal system, space group P321. At 1200°C, different diffraction patterns were also observed. These patterns were confirmed to be of the $LaAlO_3$ phase (sp. gr. R3m) (Fig. 5 (d)). And at 1300°C, this $LaAlO_3$ phase became the dominant phase amongst the mixed phases.

The crystallites grow with temperature. TEM morphology observation in Fig. 6 also verifies these phenomena. After the incipient crystallites appear, the primary particle size gradually increases; e.g., when the calcining temperature is elevated from 800°C to 1000°C, the primary particle size increases. Similarly, the crystallinity of the powders also increases with temperature. In our research, a slight difference in its feature was observed. These amorphous particles with nm size (Fig. 6 (a)) was connected and formed large amorphous particle with several grains with certain

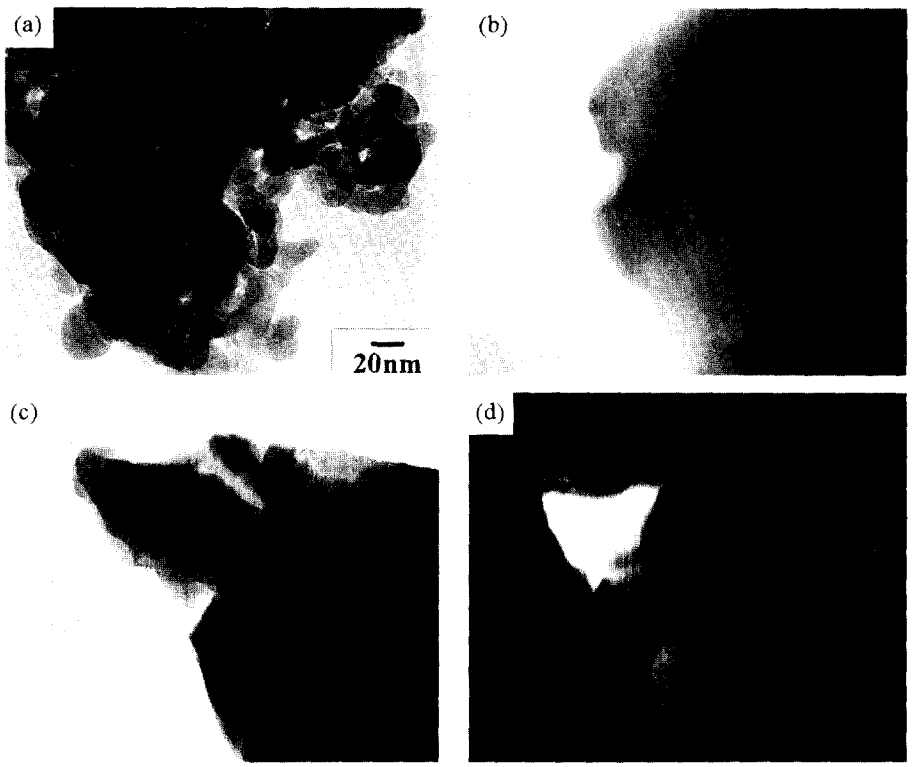

Fig. 6. TEM micrographs of (a) powder precursor and powders calcined at (b) 800°C, (c) 900°C for 3 h and (d) dark field image at 900°C.

hundreds nm in size (Fig. 6 (b)). And then, this grain was crystallized with increasing temperature. Separate grain was observed in Fig. 6 (d) by dark field image.

4. Conclusions

$La_3Al_5SiO_{14}$ powders were synthesized by the polymerized complex method. This phase, which can be retained up to 1100°C, seems to be a stable up to 1100°C. Upon increasing the calcining temperature, the $La_3Al_5SiO_{14}$ phase transforms to a $LaAlO_3$ phase above 1200°C. The crystallization process of $La_3Al_5SiO_{14}$ phase via the precursor matrix can be depicted by the following several stages:

- Before 800°C, only an amorphous phase can be obtained.
- At about 900°C, incipient crystallites of $La_3Al_5SiO_{14}$ appear. With an increase in temperature, crystallites of the phase grow and are stable up to 1100°C.
- At above 1200°C, the $La_3Al_5SiO_{14}$ phase is transformed to the $LaAlO_3$ phase.

Acknowledgements

This work was supported by the Korea Science and Engineering Foundation (KOSEF) through the Ceramic Processing Research Center (CPRC) at Hanyang University.

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