Synthesis of Langasite Powder by a Chemical Route

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Abstract Langasite($La_3Ga_5SiO_{14}$, LGS) powder was prepared by a polymerized complex method based on the Pechini-type reaction. A mixed solution of ethylene glycol(EG), citric acid(CA), lanthanum, gallium and silicon ions, with a molar ratio of EG:CA:La:Ga:Si = 100:25:3:5:1, was polymerized to form a transparent resin, which was used as a precursor for the synthesis of LGS. X-ray diffraction(XRD) patterns indicated that the LGS phase could be formed by the heat-treatment in air at 1000℃ for 3hrs.

Introduction

Langasite(LGS) is a new piezoelectric material which exhibits intermediate properties of piezoelectricity between those of quartz and lithium tantalate[1-2]. LGS crystal has been grown and investigated for laser devices since the 1980s in Russia[3]. It has been studied for the application of SAW, BAW and resonator devices, due to it's acoustic characteristics[4-6].

The polymeric precursor process based on the Pechini-type reaction[7] has recently received considerable attention because of its relatively simple synthesis procedure. One of the advantages of this technique for the synthesis of LGS has resulted from the fact that a mixed-metal citric acid complex with a stoichiometric ratio of 3La : 5Ga : Si can be formed and maintain in a polyester-based resin without any

significant changes from its stoichiometry.

In this study, a simple polymerized complex method, based on the polyesterification between citric acid and ethylene glycol[7,8] was successfully used to synthesize the LGS powder.

Experimental Procedure

The polymerized complex method for the synthesis of LGS powder was summarized in Fig. 1. 0.01 mol Tetraorthosilicate(TEOS, $(C_2H_5O)_4Si$) was mixed with 1 mol ethylene glycol(EG, $OHCH_2CH_2OH$) and then, the addition of 0.25 mol anhydrous citric acid(CA, $HOOCCH_2C(OH)(COOH)CH_2COOH$) to this solution was followed. After achieving complete dissolution, lanthanum nitrate($La(NO_3)_3 \cdot 6H_2O$) of 0.03 mol was added. Finally, gallium nitrate($Ga(NO_3)_3 \cdot nH_2O$) of 0.05 mol was added and dissolved at 50℃ for 2hrs until it became transparent. Again, this clear solution was heated at 100℃ to promote polymerization and remove excess solvents. By heating at 100℃ for several hours, the solution became more viscous, with a change in color from colorless to deep yellow, and finally it gelled into a transparent brown resin. No visible formation of precipitation or turbidity was observed during the polymerization and the gelation. The heat-treatment of the resin at 350℃ for 3hrs in an electric furnace resulted in a black solid mass. The powder, thus, obtained was heat-treated at 1000~1300℃ for 3hrs and 5hrs in air on an Al_2O_3 boat, followed by a furnace cooling to room temperature. Thermogravimetric-differential thermal analysis(TG-DTA) and powder XRD were performed to characterize the thermal properties and the phase identification of the powder. Scanning electron microscopy(SEM) was used to investigate the particle morphology.

Results and Discussions

Fig. 2 shows TG-DTA curves of LGS precursor fired in air. The TG curve(Fig. 2(a)) indicates a continuously small weight loss up to ~270℃, mostly due to dehydration and evaporation of volatile organic components, and another larger weight loss extending up to ~550℃, due to decomposition of organics involved in the precursor. A relatively weak exotherm curve at ~650 and ~770℃(marked with an arrow) in the DTA curve(Fig. 2(b)) can be probably be attributed to the onset of crystallization into LGS.

The XRD patterns of the starting powder precursor and of powders calcined in air

at three different temperatures for 3hrs and 5hrs are shown in Fig. 3 in a 2θ range of 20~60°. The starting powder precursor was primarily amorphous phase as shown in the XRD in Fig. 3(a). Crystallization had begun during the heat treatment of the powder precursor in air at 1000℃ for 3hrs(Fig. 3(b)). The XRD patterns in the Fig. 3(b)~(d) exhibited a LGS. No secondary phases, such as $LaGaO_3$ phases, La_2O_3, Ga_2O_3, or SiO_2 were observed.

A series of SEM micrographs(Fig. 4) reveals the morphological changes that occurred during the calcination of the polymeric precursor. SEM micrographs of the calcined powders that were fired in air at 1200℃ for 3hrs(a), for 5hrs(b), at 1300℃ for 3hrs(c) were shown in Fig. 4. In Fig. 4(a), it can be observed that particles keep their initial morphology after they were ground. Fig. 4(b) and (c) show spherical particles formed to minimize surface energy. Fig 4(c) shows initial neck growth in which the average particle size increased with calcined temperature. It seems that sintering has reached a certain extent without densification.

Conclusion

The polymerized complex method has been used successfully to synthesize the LGS powder. Based on the XRD-diffraction pattern, LGS was formed directly through single-step decomposition of the powder precursor, without significant phase segregation of the individual metals, and thus obtained the complete molecular-level mixing of cations in the Pechini-type polymerized complex method. Substitution of Al and Y for Ga and La respectively in the synthesis of different kinds of langasite type materials are under investigation.

References

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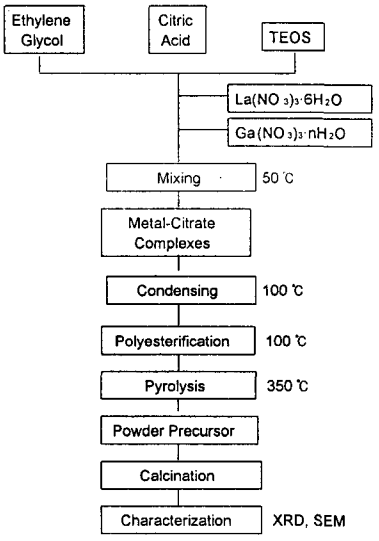
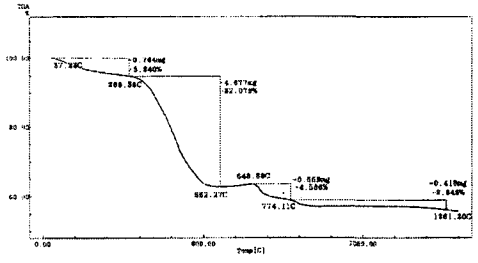
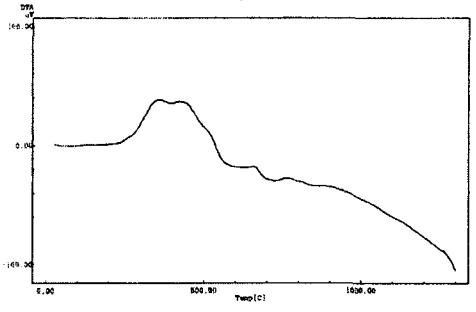


Fig. 1. Flow chart for preparing Langasite by the polymerized complex method.



(a) TGA curve



(b) DTA curve

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

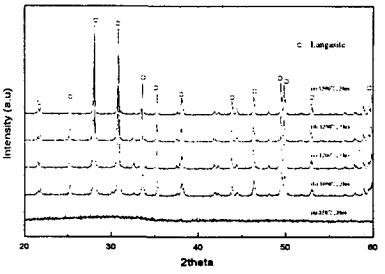
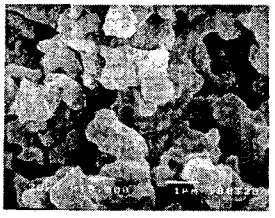
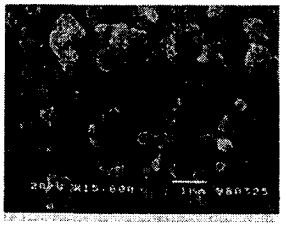


Fig. 3. X-ray diffraction patterns of products obtained by heating the precursor in air at 1000℃ for 3hrs(a), 1200℃ for 3hrs(b), 1200℃ for 5hrs(c), and 1300℃ for 3hrs(d).



(a)



(b)

(c)

Fig. 4. SEM micrographs of the calcined powder fired in air at 1200℃ for 3hrs(a), 1200℃ for 5hrs(b), and 1300℃ for 3hrs(c).