## Congruency and Liquid Immiscibility in Langasite-type Crystal with Four Elements

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This work confirms the congruency of langasite-type crystal with four elements (Ca<sub>3</sub>TaGa<sub>3</sub>Si<sub>2</sub>O<sub>14</sub>, CTGS). Secondary phase is observed during growth of bulk crystal of CTGS, which is attributed to liquid immiscibility of CTGS melt.

## **Congruency of CTGS**

Langasite-type (LGS-type) crystal with  $A_3BC_3D_2O_{14}$  structure has been intensively studied as a group of piezoelectric crystal. The well-known langasite-type crystal with three elements, such as langasite (LGS, La<sub>3</sub>Ga<sub>5</sub>SiO<sub>14</sub>) and langatate (LTG, La<sub>3</sub>Ta<sub>0.5</sub>Ga<sub>5.5</sub>O<sub>14</sub>) were found to be incongruent materials, which lead to formation of secondary phase and degradation of the quality of bulk crystals. Ca<sub>3</sub>TaGa<sub>3</sub>Si<sub>2</sub>O<sub>14</sub> (CTGS), known as langasite-type crystal with four elements, has an ordered structure and is regarded as promising material in high temperature piezoelectric crystal.

Stoichiometric CTGS (s-CTGS) compound was thoroughly sintered at 1370  $^{\circ}$ C for 48 hours. Melting and solidification process of s-CTGS sintered material was investigated by differential thermal analysis (DTA). Heated up to 1650  $^{\circ}$ C, there was only one pair of endothermic and exothermic peak in the heating and cooling process, respectively. This result was a direct evidence to assert CTGS to be a congruent material.

## Liquid immiscibility in CTGS melt

Some studies reported that s-CTGS was heated up to 1490  $^{\circ}$ C and one endothermic peak and two exothermic peaks were observed. Bulk crystal of CTGS was grown by a µ-pulling down method. A secondary phase with the composition of Ca-Ta-Ga oxide was observed by electron probe micro-analyzer (EPMA). The secondary phase appeared at the very beginning of the crystal growth. It was thought that the extra exothermic peak in DTA measurement and secondary phase in the bulk crystal were due to incongruency or eutectic reaction, but they have been deniedy by our experiments described above.

Liquid immiscibility was reported in silicate liquids. The presence of liquid immiscibility could explain the difference between the 1650 °C and the 1490 °C case: s-CTGS melt cooling down from 1500 °C had a liquid-phase separation before solidification process starts and differentiated into a Si-poor melt and a Si-rich one (Fig.1 and 2), consequently a secondary phase was observed and identified to be a Ca-Ta-Ga oxide. In contrast, the melt cooling down from 1650 °C did not experience phase seperation but directly reached the CTGS liquidus line. The secondary phase in the bulk crystal could crystallize from the Si-poor (Ga-rich) melt, which is attributed to liquid immiscibility.



Fig.1 schematic phase diagram of CTGS

Fig.2 Flow chart of the solidification process in CTGS melt

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