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Effect of $Al(OH)_3$ Addition on β-$LiAlO_2$ Crystal Growth

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Crystal growth of rod-shaped β-$LiAlO_2$ was previously reported by us, and the rod-shaped β-$LiAlO_2$ crystals were 1.5 μm in diameter and 10 to 15 μm long. In the present study needle-shaped β-$LiAlO_2$ crystals which were thinner and had larger aspect ratios (length/diameter) than the rod-shaped β-$LiAlO_2$ crystals were grown by using LiOH–Al_2O_3–$Al(OH)_3$–NaOH as the raw material. These crystals were 0.7 to 1 μm in diameter, 9 to 13 μm long, and had aspect ratios of about 10 to 13. [Key words: lithium, aluminates, crystal growth, shaping, aspect ratio.]

I. Introduction

Fuel cells have attracted special interest recently as a future highly effective method of generating electric energy.[1–3] For this application, $LiAlO_2$ crystals which are inert against alkali carbonate are desirable as a reinforcement material for the prevention of cracks in the cooling process of alkali carbonate, which is the electrolyte of molten-carbonate fuel cells. Especially long rod-shaped, needle-shaped, or fibrous $LiAlO_2$ crystals forming a fine porous structure are desirable as a reinforcement for the electrolyte. We have already reported on long rod-shaped β-$LiAlO_2$ crystals which were 1.5 μm in diameter and 10 to 15 μm long in this journal;[4] the aspect ratios of these crystals were above 6 to 10. In this paper we report on a synthesis method for thinner needle-shaped β-$LiAlO_2$ crystals having larger aspect ratios than the long rod-shaped β-$LiAlO_2$ crystals. The approximate sizes of the needle-shaped β-$LiAlO_2$ crystals reported in this paper were 0.7 to 1 μm in diameter, 9 to 13 μm long, with aspect ratios of 10 to 13 (the word "needle-shaped" was used only to distinguish β-$LiAlO_2$ crystals from the previous long rod-shaped crystals).

II. Synthesis of Needle-Shaped β-$LiAlO_2$ Crystals

The starting materials were reagent-grade $LiOH \cdot H_2O$, industrial-grade γ-Al_2O_3 (Al_2O_3 content >99.6 wt%), industrial-grade $Al(OH)_3$ ($Al(OH)_3$ content 99.5 wt%), and reagent-grade NaOH. They were weighed out in 15-g batches and mixed well (mole ratio $LiOH \cdot H_2O$:γ-Al_2O_3:$Al(OH)_3$:NaOH = 4:0.7:0.6:4.3) with 8 wt% water. The mixed hard paste was molded into test pieces (25 mm in diameter and 15 mm high). The test pieces were placed in a muffle furnace (65 wt% Al_2O_3, 31 wt% SiO_2, interior dimensions 180 mm × 80 mm × 80 mm), heated to 550°C at 5°C/min, and held for 3 h (in preliminary experiments these heating conditions were good for crystal growth). After the pieces were heated and cooled, they were dipped into water for 24 h and disentangled.

III. Experimental Results

The disentangled products were confirmed to be β-$LiAlO_2$ crystals by X-ray analysis. These needle-shaped β-$LiAlO_2$ crystals are shown in Fig. 1(A). Most of these needle-shaped crystals were 0.7 to 1 μm in diameter and 9 to 13 μm long (aspect ratios were above 10 to 13). Heating conditions and combinations of raw materials were varied extensively. The foregoing long rod-shaped β-$LiAlO_2$ crystals using LiOH–Al_2O_3–NaOH as the raw material[4] were 1.5 μm in diameter, 10 to 15 μm long, and had aspect ratios above 6 to 10. The long rod-shaped β-$LiAlO_2$ crystals are shown in Fig. 1(B). The new needle-shaped β-$LiAlO_2$ crystals were equivalent in length, thinner in diameter, and greater in aspect ratio than the long rod-shaped β-$LiAlO_2$ crystals. From these results it was determined that $Al(OH)_3$ was effective for thin crystal growth of β-$LiAlO_2$. A controlling factor for the growth of needle-shaped β-$LiAlO_2$ crystals is probably the effect of vaporization of the alkali compound liquid as was stated previously,[4] but in this case it does not explain the effect of $Al(OH)_3$ addition on this crystal growth.

IV. Conclusion

Needle-shaped β-$LiAlO_2$ crystals thinner in diameter and greater in aspect ratio than the rod-shaped β-$LiAlO_2$ crys-

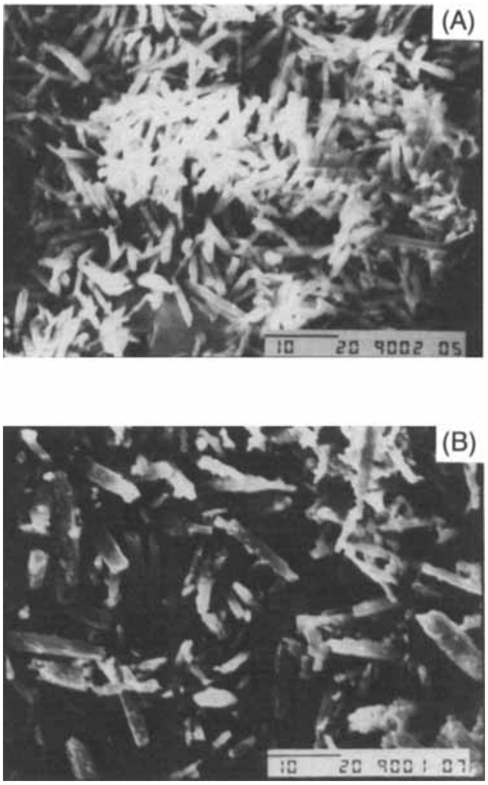

Fig. 1. Scanning electron micrograph of β-$LiAlO_2$ crystals: (A) $LiOH \cdot H_2O$:γ-Al_2O_3:$Al(OH)_3$:NaOH = 4:0.7:0.6:4.3 (mole ratio); (B) $LiOH \cdot H_2O$:γ-Al_2O_3:NaOH = 4:1:4 (mole ratio). Bar = 10 μm.

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tals using $LiOH–Al_2O_3–NaOH$ as the raw materials were synthesized by using $LiOH–Al_2O_3–Al(OH)_3–NaOH$.

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