

Morphology control of pseudobrookite-type MgTi_2O_5 powders by LiF doping

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ABSTRACT

Well-controlled fine MgTi_2O_5 powders, with pseudobrookite-type structure, are desired toward various industrial applications, however, commercial powders are hardly available to date. In this study, we focused the processing and characterization of well-controlled MgTi_2O_5 powders with/without LiF additive. MgCO_3 (basic) and TiO_2 anatase powders with/without 0.5 wt. % LiF additive were calcined in air at 1100 °C for 2 h to obtain the MgTi_2O_5 powders. SEM observation revealed that the non-doped MgTi_2O_5 powder consisted of equiaxed particles with the diameter of 0.5-1.5 μm , whereas, the LiF-doped MgTi_2O_5 powder consisted of elongated particles with the length of ~5-10 μm and the diameter of ~1.0-1.5 μm . The smooth surface of elongated MgTi_2O_5 particles demonstrates the effect of LiF doping as a flux, i.e., liquid phase formation during the reaction.

Keywords: MgTi_2O_5 ; pseudobrookite; porous ceramics; LiF, mineralizer; microstructure; elongated grains

1. INTRODUCTION

Double oxides with pseudobrookite-type structure (space group $Cmcm$ (63), Figure 1) have characteristic unidirectional low-thermal expansion along with a -axis [1]. Among the pseudobrookite-type ceramics, aluminum titanate, Al_2TiO_5 , is applied for next-generation diesel particulate filters (DPF) and so on due to its low bulk thermal expansion [2]. However, Al_2TiO_5 is thermodynamically metastable under 1200 °C and it gradually decomposes into Al_2O_3 and TiO_2 [3-5]. Furthermore, due to the strong anisotropy of thermal expansion, Al_2TiO_5 ceramics have poor mechanical properties caused by microcrack formation. Magnesium dititanate (MgTi_2O_5), with pseudobrookite-type structure, also has characteristic unidirectional low-thermal expansion, however, it is less crystallographically anisotropic and more thermally stable than Al_2TiO_5 [1]. Suzuki et al. have recently reported uniformly porous MgTi_2O_5 ceramics with 3-D network structure [6-9]. By controlling the stoichiometry and the liquid phase content, idiomorphic MgTi_2O_5 grains were formed [9].

Although well-controlled fine MgTi_2O_5 powders are desired toward various industrial applications, commercial powders are hardly available to date. From our previous study [9], LiF doping is effective to control the morphology of MgTi_2O_5 particles, however, the detail

has not yet been clarified. In this study, we focused the processing and characterization of well-controlled MgTi_2O_5 powders with/without LiF additive.

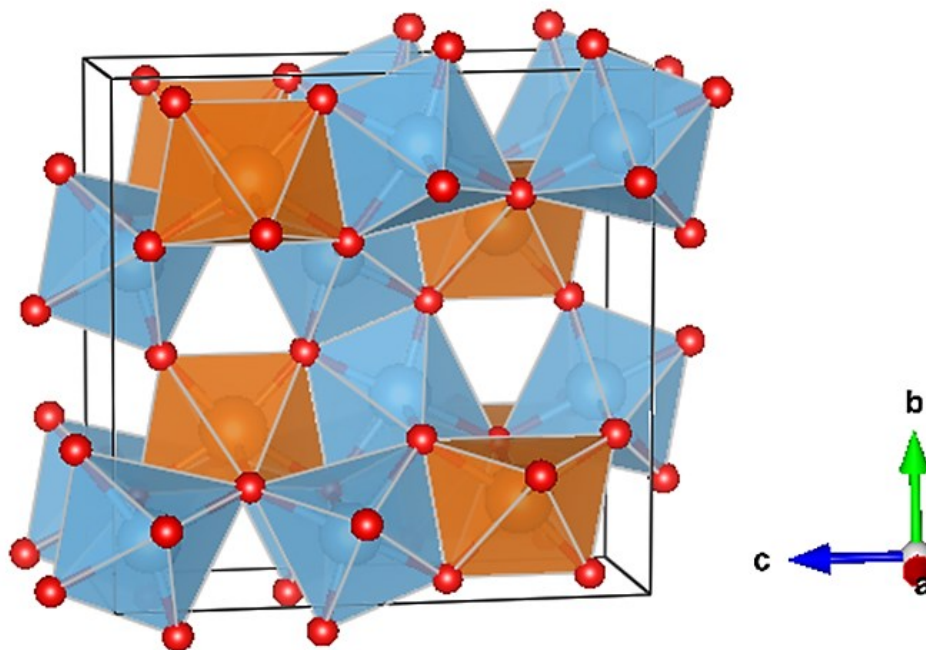


Figure 1. Crystal structure of pseudobrookite-type compound (*Cmcm* space group [1]).

2. EXPERIMENTAL

Similarly to our previous work [6,7,9], commercially available MgCO_3 (basic) powder (99.9% purity, Kojundo Chemical Laboratory Co. Ltd., Saitama, Japan), TiO_2 anatase powder (99.9% purity, Kojundo Chemical Laboratory Co. Ltd.), and LiF powder (99.9%, Wako Pure Chemical Ind., Ltd, Osaka, Japan) were used as the starting materials. LiF acts as a mineralizer. Since the MgCO_3 (basic) powder contains plenty of OH groups and H_2O molecules, quantitative analysis of the starting powder was performed by thermogravimetry and differential thermal analysis (TG-DTA). Based on the compositional calibration using TG-DTA data, MgCO_3 (basic) and TiO_2 powders (nominally, Mg:Ti = 1:2 in mole fraction) with LiF (0.5 wt% for total starting powders) were wet-ball milled in ethanol for 24 h. The mixed slurry was vacuum dried, and the dried powder was put into the oven at 80 °C for 1 night. The mixed powder was then sieved through a 150-mesh screen. The mixed powders (i.e with and without 0.5 wt% LiF) were calcined in air at 1100 °C for 2 h (the ramp rate was 5 °C/min) to obtain the MgTi_2O_5 powders. The crystal structure of obtained powders was analyzed by X-ray diffraction method (XRD, Rigaku, Multiflex, Cu- $K\alpha$, 40 kV and 40 mA). The microstructure of the powders was observed by field emission scanning electron microscopy (FE-SEM, SU-70, High High-Tech, Japan).

3. RESULTS AND DISCUSSION

Figure 2 shows XRD patterns of MgTi_2O_5 powders with and without LiF addition. The non-doped MgTi_2O_5 powder consisted of single-phase MgTi_2O_5 , whereas the LiF-doped MgTi_2O_5 powder slightly containing MgTiO_3 , which is an intermediate phase of the MgO-TiO_2 reaction system [6]. It is deduced that the intermediate MgTiO_3 phase might be also grown and somewhat stabilized with LiF doping.

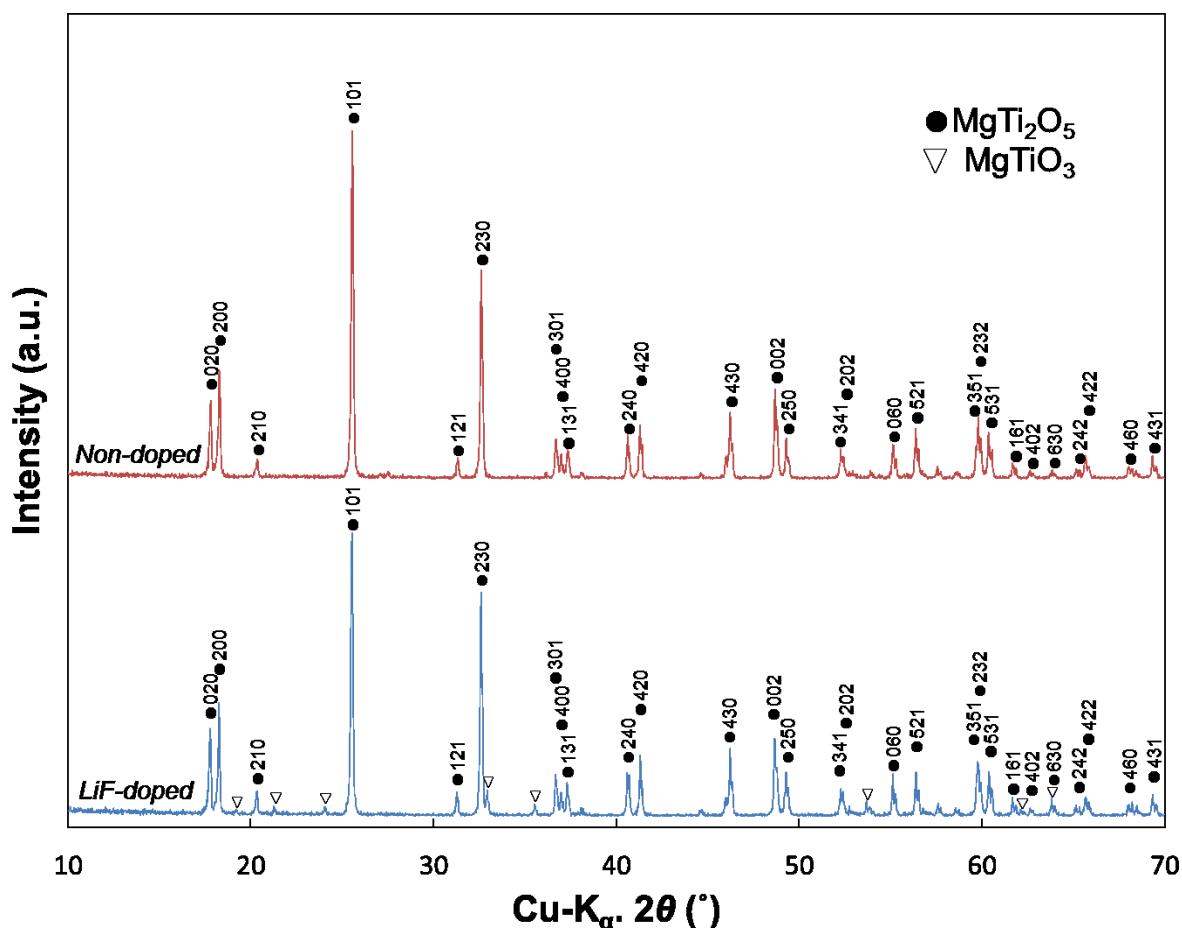


Figure 2. X-ray diffraction patterns of non-doped LiF-doped and MgTi_2O_5 powder.

Figure 3 shows SEM micrographs of MgTi_2O_5 powders with and without LiF addition. The microstructure was remarkably different between two powders. The non-doped MgTi_2O_5 powder consisted of equiaxed particles with the diameter of 0.5-1.5 μm . On the other hand, the LiF-doped MgTi_2O_5 powder consisted of elongated particles with the length of ~ 5 -10 μm and the diameter of ~ 1.0 -1.5 μm . Some equiaxed particles found in the LiF-doped MgTi_2O_5 powder can be attributed to the MgTiO_3 particles, which was in good agreement with the XRD result. The smooth surface of elongated MgTi_2O_5 particles demonstrates the effect of LiF as a mineralizer, i.e., liquid phase formation during the reaction. The liquid phase enhanced anisotropic crystal growth of the pseudobrookite phase. These elongated particles are suitable for the applications of gas or liquid filter materials with low pressure loss.

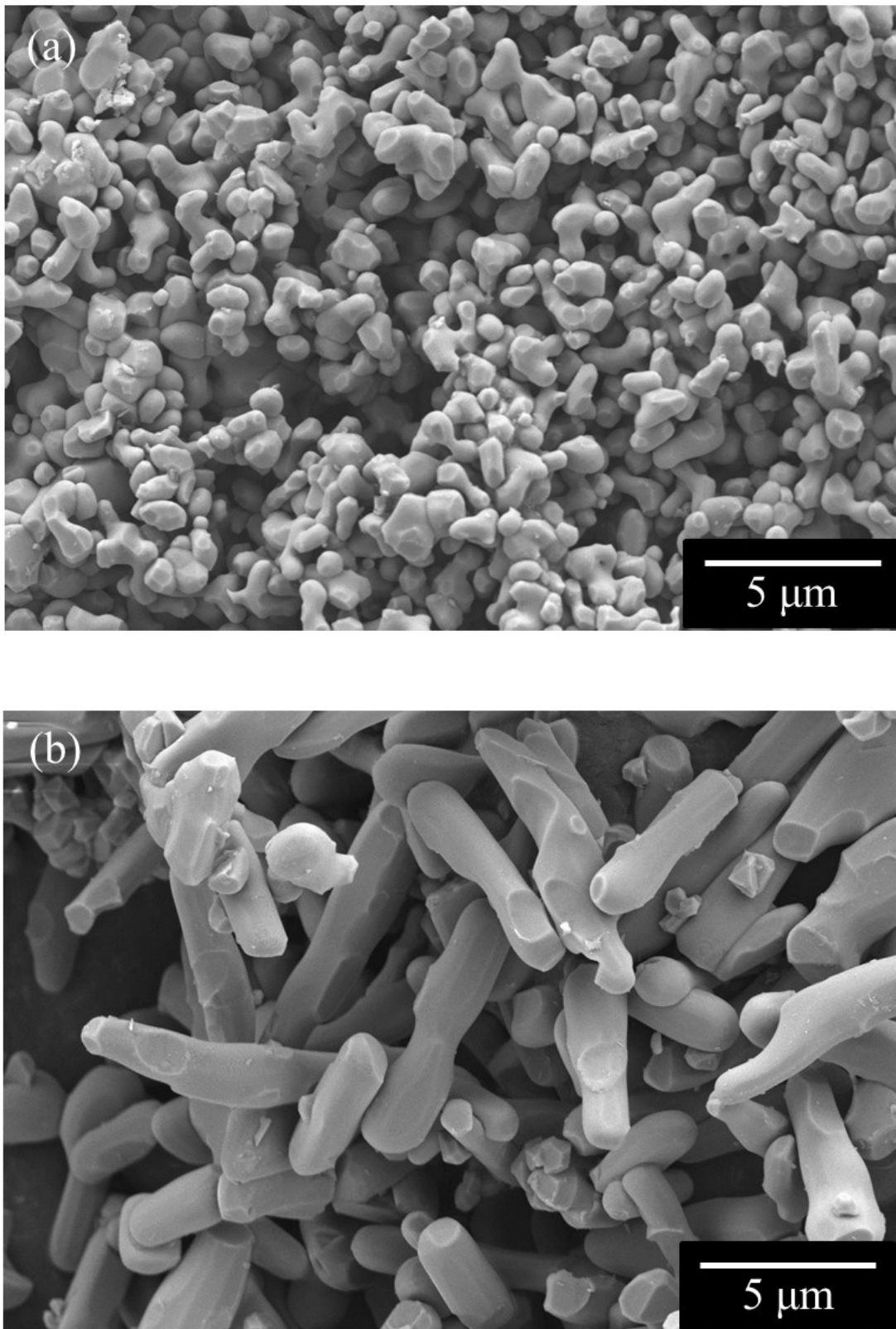


Figure 3. SEM images of (a) non-doped MgTi_2O_5 powder and (b) LiF-doped MgTi_2O_5 powder.

4. CONCLUSIONS

In this study, we synthesized well-defined MgTi_2O_5 powders from MgCO_3 (basic) and TiO_2 anatase powders with/without LiF additive. The 0.5 wt% LiF-doped MgTi_2O_5 powder was composed of elongated MgTi_2O_5 particles with the length of $\sim 5\text{-}10\ \mu\text{m}$ and the diameter of $\sim 1.0\text{-}1.5\ \mu\text{m}$. These elongated particles are suitable for the applications of gas or liquid filter materials with low pressure loss.

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References

- [1] G. Bayer, *J. Less-Common Metals* 24 (1971) 129-138.
- [2] I. J. Kim, *J. Ceram. Proc. Res.* 11 (2010) 411-418.
- [3] E. Kato, K. Daimon, J. Takahashi, *J. Am. Ceram. Soc.* 63 (1980) 355-356.
- [4] T. S. Liu, D. S. Perera, *J. Mater. Sci.*, 33 (1998) 995-1001.
- [5] S. M. Lang, C. L. Filmore, L. H. Maxwell, *J. Res. Nat. Bur. Sta.* 48 (1952) 298-312.
- [6] Y. Suzuki, M. Morimoto, *J. Ceram. Soc. Jpn.* 118 (2010) 819-822.
- [7] Y. Suzuki, M. Morimoto, *J. Ceram. Soc. Jpn.* 118 (2010) 1212-1216.
- [8] Y. Suzuki, Y. Shinoda, *Sci. Tech. Adv. Mater.* 12 (2011) no. 034301.
- [9] Y. Suzuki, T. S. Suzuki, Y. Shinoda, K. Yozhida, *Adv. Eng. Mater.* 14 (2012) 1134-1138.
- [10] NIMS AtomWork Database (<http://crystdb.nims.go.jp/>)
- [11] K. Momma and F. Izumi, *J. Appl. Crystallography* 44 (2011) 1272-1276.

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