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Preparation of the Negative Thermal Expansion Material $Zr_2SP_2O_{12}$ and Related Materials

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Abstract

Materials with a negative coefficient of thermal expansion (CTE) have been actively studied for compositing with materials with a high CTE to control the CTE. Negative thermal expansion in $Zr_2SP_2O_{12}$ operates via two main unique mechanisms: phase transition (373–453 K) and framework-type (303–373 K and 453–773 K). $Zr_2SP_2O_{12}$ is a promising material in this research field because of its relatively low CTE over a wide temperature range. This study describes the mechanism of shrinkage of $Zr_2SP_2O_{12}$ and introduces control of the CTE by elemental substitution of the Zr sites.

Key-words: *Ceramic, Crystal structure, Phase transition*

1. Introduction

Thermal expansion is a fundamental property of a material. The coefficient of thermal expansion (CTE) varies greatly among materials, ranging from 10 to 30 ppm/K for metals, 50 to 200 ppm/K for plastics and resins, and 1 to 25 ppm/K for ceramics and glass. Thermal expansion has long been used for a wide range of purposes, from consumer to industrial applications, such as thermometers and bimetals. However, problems such as the elongation of railroad rails and the destruction of tableware through thermal shock are also widely known. In recent years, slight thermal expansion has become a problem in areas such as optical devices and semiconductor manufacturing, where precise positioning and dimensional control of components are required. In devices that combine multiple materials, differences in the CTE of each material can lead to serious problems such as interface delamination and wire breakage[1)]. Therefore, various near-zero thermal expansion materials and thermal expansion control technologies have been studied. Invar alloys[2)], glass[3)], cordierite[4,5)], etc., are widely known to exhibit near-zero thermal expansion in a single phase and are applied in industrial and consumer products[6)]. However, for materials in which control of the CTE is difficult in the single phase, thermal expansion can be suppressed by compositing with filler materials having a low CTE[7)]. In particular, materials with a negative CTE, which shrink as the temperature increases, can be used as filler materials because it is expected that at low loadings, they can cancel the thermal expansion of the structural material, thereby controlling only the thermal expansion rate while maintaining the properties of the base material[8-14)]. Since the 2000s, many important materials with negative CTE have been reported, and the field has gained new momentum[15)]. Our research group reported $Zr_2SP_2O_{12}$ as a new material. $Zr_2SP_2O_{12}$ has a wide temperature range and a low CTE because of multiple shrinkage mechanisms. Therefore, it is considered an industrially promising material. This study introduces $Zr_2SP_2O_{12}$ and related materials.

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〔経歴〕 平成13年名古屋工業大学大学院博士課程前期修了。平成15年東京工業大学大学院博士課程後期修了。博士（工学）。平成18年産業技術総合研究所産総研特別研究員。平成20年東京工業大学特任助教，助教を経て，平成31年から現職。

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2. Mechanism of negative thermal expansion

2.1 Phase transition-type mechanisms

The main mechanisms of negative CTE can be classified into phase transitions and framework-type. The phase transition-type is based on the volume change before and after the phase transition (**Fig. 1**)[14)]. Generally, phase transitions and volume changes occur at specific temperatures. However, the partial substitution of elements (or introduction of defects) into a material leads to a volume change within the temperature range. The phase transition-type pertains to a negative thermal expansion material that undergoes this volume change.