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Mechanism of the negative thermal expansion in NASICON structures from theoretical calculations and experiments

Y. Mochizuki*,1), R. Kaneda1), S. Bae2), T. Isobe1), S. Matsushita1), and A. Nakajima1)
1) Tokyo Institute of Technology, O-okayama, Meguro, Tokyo, Japan
2) Yokohama National University

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Corresponding author*: mochizuki.y.af@m.titech.ac.jp

Abstract

Elucidation of negative thermal expansion (NTE) behavior has presented a challenge ever since its discovery. Here, by using the quasi-harmonic approximated phonon calculations and high-temperature XRD analyses, we calculated and measured the thermal expansion coefficient of $KZr_2P_3O_{12}$, which is a NASICON-type NTE material. We found that a Brillouin-zone-center phonon largely contributes the NTE behavior of $KZr_2P_3O_{12}$.

1. Introduction

Negative-thermal-expansion materials have attracted considerable attention because they contribute to sustain the lifespan of largely expanding materials and also because of their fascinating and counter-intuitive thermal properties. The well-known and representative NTE materials are Si [1], ReO_3 [2], ScF_3 [3] ZrW_2O_8 [4] and $KZr_2P_3O_{12}$ [5]. Since the reports of NTE in various materials in the past few decades, it has been widely known that the mechanism for NTE is the transverse acoustic phonon modes, which have negative Grüneisen parameters. However, the detailed mechanisms for the NTE properties are uncovered ever since now. Here, we report our progress for elucidating the microscopic origin of NTE in Si, ReO_3, and $KZr_2P_3O_{12}$.

2. Calculational and Experimental methods

Our first-principles calculations were performed by using the projector augmented-wave method [6], and the PBEsol functional within the generalized gradient approximation [7] as implemented in VASP [8]. The phonon band structures were derived from the calculated force constants using PHONOPY [9]. The polycrystalline $KZr_2P_3O_{12}$ was synthesized by liquid-phase method. First, we prepared the precursor by dissolving $(NH_4)_2HPO_4$, $ZrCl_2O\cdot 8H_2O$, and KNO_3 into deionized water, and stirred at 80°C for 4 hours. Then we dried the obtained product at 150°C for 4 hours and calcined the dried powder for 800°C for 4 hours, resulting in preparation of polycrystalline $KZr_2P_3O_{12}$. The Rietveld analyses were performed by using RIETAN [10].

3. Results and discussion

As shown in Fig. 1, we present the calculation results of phonon band with Grüneisen parameters for Si, ReO_3, and $KZr_2P_3O_{12}$. From Figs. 1(a), 1(b), 1(d), 1(e), one can see that the zone-boundary phonon modes in Si and ReO_3 generate negative Grüneisen parameters, triggering the NTE. In Si, the most important phonons for realizing NTE are the atomic vibration eigenvectors which transform as irreducible representations (irreps) X_4 and L_3^-, while in ReO_3, the most important phonons for the NTE are the eigenvectors transforming as irreps M_2^+ and R_5^-, the phonon modes of which respectively correspond to the ReO_6 in-phase and out-of-phase octahedral rotations. Note that these zone-*boundary* phonon modes of Si and ReO_3 are low-energy transverse acoustic phonon modes. Intriguingly, a Brillouin-zone-*center* mode transforming as irrep Γ_2^+ in $KZr_2P_3O_{12}$ contributes to its NTE the most as shown in Figs. 1(c), 1(f). Our results suggest that not all NTE behaviors are originated from zone-boundary phonon modes.

4. Conclusions

The thermal expansion coefficient of $KZr_2P_3O_{12}$ was calculated and measured respectively by phonon calculation and high-temperature XRD measurement. We found that a Brillouin-zone-center phonon which transforms as Γ_2^+ contributes to the NTE behavior of $KZr_2P_3O_{12}$ the most.

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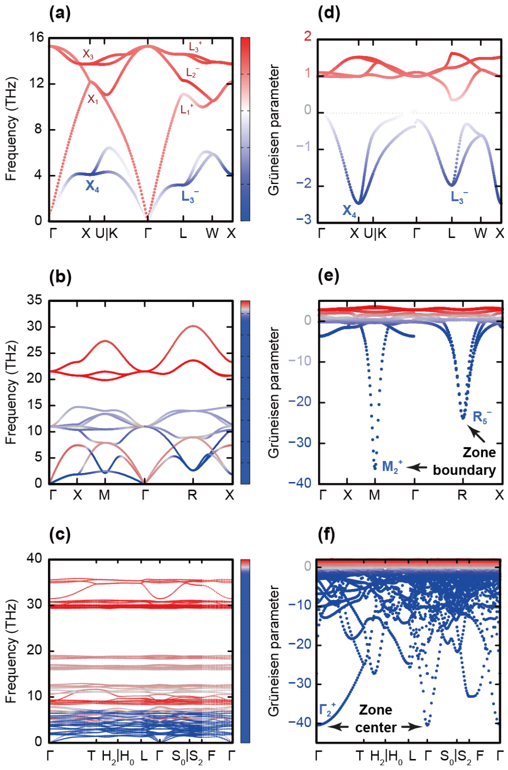

Fig 1. Calculated phonon bands for (a) Si, (b) ReO_3, and (c) $KZr_2P_3O_{12}$ and Grüneisen parameters for (d) Si, (e) ReO_3, and (f) $KZr_2P_3O_{12}$. The red and blue respectively indicate the degrees of positive and negative values of Grüneisen parameters.

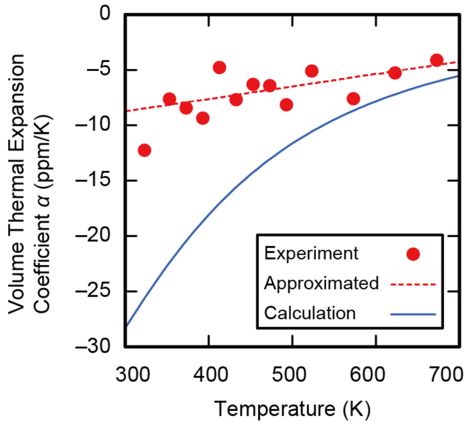

Fig 2. Theoretical (blue) and experimental (red) thermal expansion coefficients for $KZr_2P_3O_{12}$. The red broken line is derived by least-square method.