Direct observation of negative thermal expansion in $\text{SrCu}_3\text{Fe}_4\text{O}_{12}$

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We report a direct observation of the negative thermal expansion in an iron-based perovskite oxide $\text{SrCu}_3\text{Fe}_4\text{O}_{12}$ by using a thermomechanical analyzer and strain gauge. Reversibility and small thermal hysteresis in the negative thermal expansion temperature range demonstrate that the negative thermal expansion of this compound is attributed to second-order phase transition.

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1. Introduction

Negative thermal expansion (NTE) materials, which show volume contraction upon warming (volume expansion upon cooling), have been extensively investigated because of their potential utility in precision mechanical engineering and optics.^{1,2)} Combination of NTE materials with conventional materials having a positive thermal expansion may help suppress degradation resulting from volume expansion and contraction during thermal cycles and aid in precise control of the operating life. Recently, several novel NTE materials with large negative coefficients of linear thermal expansion (CTE, α_L), on the order of 10^{-5} K^{-1} , were reported. For instance, antiperovskite-type nitrides $\text{Mn}_3(\text{Cu}, \text{Ge})\text{N}$ showed a large NTE ($\alpha_L = -1.6 \times 10^{-5} \text{ K}^{-1}$) near room temperature, which was achieved by relaxation of the magnetovolume effect of the parent compound Mn_3CuN .³⁾ A perovskite-type oxide $(\text{Bi}, \text{La})\text{NiO}_3$ exhibited a significantly high NTE ($\alpha_L = -8.2 \times 10^{-5} \text{ K}^{-1}$) above room temperature because of the first-order phase transition temperature, at which intersite charge transfer (simplified as $\text{Bi}^{4+} + \text{Ni}^{2+} \rightarrow \text{Bi}^{3+} + \text{Ni}^{3+}$ on heating) is dominant.⁴⁾

$\text{SrCu}_3\text{Fe}_4\text{O}_{12}$ (SCFO) belongs to the class of cubic A-site ordered perovskites $\text{ACu}_3\text{Fe}_4\text{O}_{12}$ ($A = \text{Ca}, \text{Sr}, \text{La}, \text{ and } \text{Y}$)⁵⁻⁸⁾ with 1:3-type ordering of the A-site cations (see the crystal structure in Fig. 1).⁹⁾ Coexistence of the two transition metal (Cu and Fe) ions at different crystallographic sites in $\text{ACu}_3\text{Fe}_4\text{O}_{12}$ induces intriguing electronic interactions between these ions, such as intersite charge transfer and magnetic superexchange interactions. Rietveld refinement of SCFO based on synchrotron X-ray powder diffraction (SXRD) revealed drastic changes in metal–oxygen bond lengths, that is, gradual elongation (shrinkage) of the Cu–O (Fe–O) bond upon heating in the temperature range 170–270 K, leading to an NTE ($\alpha_L = -2.3 \times 10^{-5} \text{ K}^{-1}$).⁶⁾ Bond valence sum calculations suggested that the above-mentioned structural trans-

Fig. 1. Crystal structure of $\text{SrCu}_3\text{Fe}_4\text{O}_{12}$. The light-blue, dark-blue, brown, and red spheres represent Sr, Cu, Fe, and O atoms, respectively.

formations correspond to a crossover-like intersite charge transfer between the Cu and Fe ions ($\text{Cu}^{3+} + \text{Fe}^{3+} \rightarrow \text{Cu}^{2+} + \text{Fe}^{4+}$ on heating), resulting in an NTE in this temperature range.

In this study, we show a direct observation of the NTE of SCFO by dilatometric analysis. The dilatometric data demonstrated a negative CTE of $\alpha_L = -7 \times 10^{-6} \text{ K}^{-1}$. Reversibility and significantly small thermal hysteresis in the NTE temperature range were also confirmed by the dilatometric measurements.

2. Experimental procedure

The precursor of $\text{SrCu}_3\text{Fe}_4\text{O}_{12}$ was prepared by the polymerized complex method in the same manner described in a previous report.⁶⁾ The precursor powder with a nominal formula of $\text{SrCu}_3\text{Fe}_4\text{O}_{10}$ was mixed with KClO_4 (99.9%) in a molar ratio of 2:1 in order to compensate for the oxygen stoichiometry. The mixture was compressed to 15 GPa using a Kawai-type high-pressure

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apparatus, heated to 1273 K for 30 min, maintained at this temperature for 30 min, and quenched to ambient temperature. The pressure was slowly released after the heat treatment. The obtained powder was washed with water to remove the residual KCl. Pelletized samples for dilatometric measurements were prepared by sintering the above-mentioned powder at 15 GPa and 1273 K for 30 min. The obtained pellets were ~ 2 mm in diameter and 1–2 mm in height.

X-ray powder diffraction (XRD) patterns were collected over the temperature range 100–450 K with a 10 K step, in a RIGAKU Ultima IV X-ray diffractometer using $\text{Cu K}\alpha$ radiation. Synchrotron X-ray diffraction (SXRD) pattern at room temperature was collected using a Debye–Scherrer camera installed at the BL02B2 beamline of SPring-8. Lattice constants and phase fraction were refined by Rietveld refinement using the program RIETAN-FP.¹⁰⁾ Linear thermal expansion of the sintered pellets was measured by means of two kinds of dilatometric methods. Thermomechanical analysis (TMA) measurements were conducted over the temperature range 125–400 K using a thermomechanical analyzer RIGAKU TMA8310 system. Strain gauge (SG) measurements were performed in the temperature range 4–400 K using a KYOWA-type KFL strain gauge on a He refrigerator PASCAL 101D HE. The cooling/heating rate in the TMA and SG measurements were ~ 3.1 and ~ 1.6 K/s, respectively.

3. Results and discussion

Figure 2 shows the room-temperature SXRD pattern and Rietveld refinement result of the sample prepared by grinding the sintered pellet after the TMA and SG measurements. The reliability factors ($R_{\text{wp}} = 3.692\%$, $R_{\text{B}} = 1.699\%$) and goodness-of-fit ($S = 1.0025$) indicate that the refinement result is appropriate. The primary phase could be indexed in the cubic A-site ordered perovskite structure with the space group $Im\bar{3}$. The refined value of the lattice constant a was 7.36053(19) Å, which roughly agreed with that mentioned in a previous report (7.34921 Å).⁶⁾ Several impurities such as CuO, $\alpha\text{-Fe}_2\text{O}_3$, and unknown phase(s) were observed (see the inset of Fig. 2). The volume fractions of SCFO, CuO, and $\alpha\text{-Fe}_2\text{O}_3$ estimated from the Rietveld refinement were 71.14, 15.45, and 13.42%, respectively.

Fig. 2. XRD pattern of $\text{SrCu}_3\text{Fe}_4\text{O}_{12}$ measured at room temperature. The black circles and red line represent the observed and calculated profiles, respectively. The blue line in the bottom shows the difference between the observation and calculation. The vertical bars display the Bragg reflection positions for $\text{SrCu}_3\text{Fe}_4\text{O}_{12}$, CuO, and $\alpha\text{-Fe}_2\text{O}_3$ from top to bottom, respectively. The inset shows the enlarged pattern in the selected 2θ range (6.3–11.5°). The asterisks represent the Bragg reflection positions for unknown phases.

Figure 3(a) shows the temperature dependence of the linear thermal expansion $dL/L_{400\text{K}}$ of SCFO, as determined by SXRD (data from Ref. 6), XRD, TMA, and SG measurements. The XRD data in this study show an NTE at about the same temperature range as the SXRD data. The CTE, obtained from a linear fitting of the XRD data between 230 and 270 K, was $-2.3 \times 10^{-5} \text{ K}^{-1}$ [see Fig. 3(b)], which is consistent with a previous report.⁶⁾ The continuous change in the linear thermal expansion suggested the second-order-type phase transformation. The TMA and SG data also demonstrated an NTE over a similar temperature range as the SXRD and XRD, which are direct observations of the NTE for SCFO. The magnitude of the NTE was smaller than that obtained from the SXRD and XRD data; the α_L values were calculated as -7.4×10^{-6} and $-6.5 \times 10^{-6} \text{ K}^{-1}$ from the TMA and SG data, respectively. This is mainly because the TMA

Fig. 3. (a) Linear thermal expansion $dL/L_{400\text{K}}$ of $\text{SrCu}_3\text{Fe}_4\text{O}_{12}$ measured by means of SXRD (Ref. 6, heating), XRD (heating), TMA (cooling), and SG (heating). (b) Linear thermal expansion $dL/L_{400\text{K}}$ of $\text{SrCu}_3\text{Fe}_4\text{O}_{12}$, CuO, and $\alpha\text{-Fe}_2\text{O}_3$ phases of the sample. The lines represent the linear fitting results. (c) Linear thermal expansion $dL/L_{300\text{K}}$ of $\text{SrCu}_3\text{Fe}_4\text{O}_{12}$ measured using strain gauge upon cooling and heating.

and SG methods involve measurements on the gross CTE of the sample pellet, which includes the impurity phases with a positive CTE. The Rietveld refinement results gave a positive CTE for CuO ($5.5 \times 10^{-6} \text{ K}^{-1}$) and $\alpha\text{-Fe}_2\text{O}_3$ ($6.8 \times 10^{-6} \text{ K}^{-1}$) in the temperature range 200–300 K [Fig. 3(b)]. These components and the unidentified phases significantly suppress the bulk NTE. The bulk CTE of the sample was calculated to ca. $-1.5 \times 10^{-5} \text{ K}^{-1}$, in accordance with the formula: $\alpha = (\sum_i^n \alpha_i E_i V_i) / (\sum_i^n E_i V_i)$, where α_i , E_i , and V_i represent CTE, Young's modulus, and volume fraction for the i -th component, respectively, and E_i for all the components were assumed to the same value. This CTE value remains larger than those obtained from the TMA and SG data. One of the reasons is the simple assumption of the Young's modulus. Another possible reasons are the sinterability, grain boundary, and porosity of the sample, as pointed out in the case of $(\text{Bi,L a})\text{NiO}_3$.⁴⁾

Figure 3(c) shows the temperature dependence of the linear thermal expansion $dL/L_{300\text{K}}$ of SCFO upon cooling and heating, as determined from the SG measurements. In both the cooling and heating processes, almost identical NTE behaviors were observed, confirming that the NTE of SCFO is reversible. Furthermore, the thermal hysteresis was negligible ($\sim 2.5 \text{ K}$) in the NTE temperature range. This was because the NTE of SCFO was attributed to the second-order phase transition, as indicated by XRD.

The above results may augment the advantages of SCFO in practical applications, although the sample preparation process is complex. Since SCFO retains a cubic symmetry over a wide temperature range of 80–450 K, isotropic expansion and contraction can be expected. In addition, the thermal hysteresis of SCFO is considerably small. These properties may help in preventing the generation of microcracks during thermal cycles. Further modification such as chemical substitution may improve the NTE characteristics of this compound.

4. Summary

Dilatometric analysis for the direct observation of the negative thermal expansion in $\text{SrCu}_3\text{Fe}_4\text{O}_{12}$ was performed by using a

thermomechanical analyzer and strain gauge. Reversibility and small thermal hysteresis in the negative thermal expansion temperature range were observed, leading us to conclude that the negative thermal expansion of $\text{SrCu}_3\text{Fe}_4\text{O}_{12}$ is attributed to second-order phase transition.

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