Giant Negative Thermal Expansion Materials

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Suppression of thermal expansion is of great importance for industry. Negative thermal expansion (NTE) materials which shrink on heating and expand on cooling are therefore attracting keen attention. It is also known that $PbTiO_3$ exhibits a negative thermal expansion (NTE) at the ferroelectric to palaelectric transition. $PbVO_3$ has a largely distorted $PbTiO_3$-type structure due to the d_{xy} orbital ordering of V^{4+} ion with d^1 electronic configuration. The large tetragonal distortion with a c/a ratio of 1.23 prohibits a transition to the palaelectric phase on heating, but the distortion decreases with electron doping by Bi^{3+} or La^{3+} substitution for Pb^{2+} and $Pb_{0.76}Bi_{0.20}La_{0.04}VO_3$ exhibits NTE with a volume contraction as large as 6.7% around room temperature [1].

$BiNiO_3$ is an antiferromagnetic insulator synthesized at 6GPa with a unique charge distribution of $Bi^{3+}_{0.5}Bi^{5+}_{0.5}Ni^{2+}O_3$ [2]. It shows a 2.6% volume reduction under pressure due to a Bi/Ni charge transfer accompanied by an insulator to metal transition [3]. The charge transfer transition is shifted to ambient pressure through lanthanum substitution for Bi or Fe substitution for Ni. Because the low-temperature and high-temperature phases coexist changing their fractions each other in a wide temperature range above room temperature, the weighted volume smoothly decreases on heating [4,5]. The coefficient of thermal expansion (CTE) of $BiNi_{0.85}Fe_{0.15}O_3$ reaches -187×10^{-6} K^{-1} and it is demonstrated that 18 vol% addition of the present compound compensates for the thermal expansion of epoxy resin.

These two phase transitions simultaneously take place in heavily Fe doped $BiNi_{1-x}Fe_xO_3$ ($0.25 \leq x \leq 0.5$) [6].

References

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