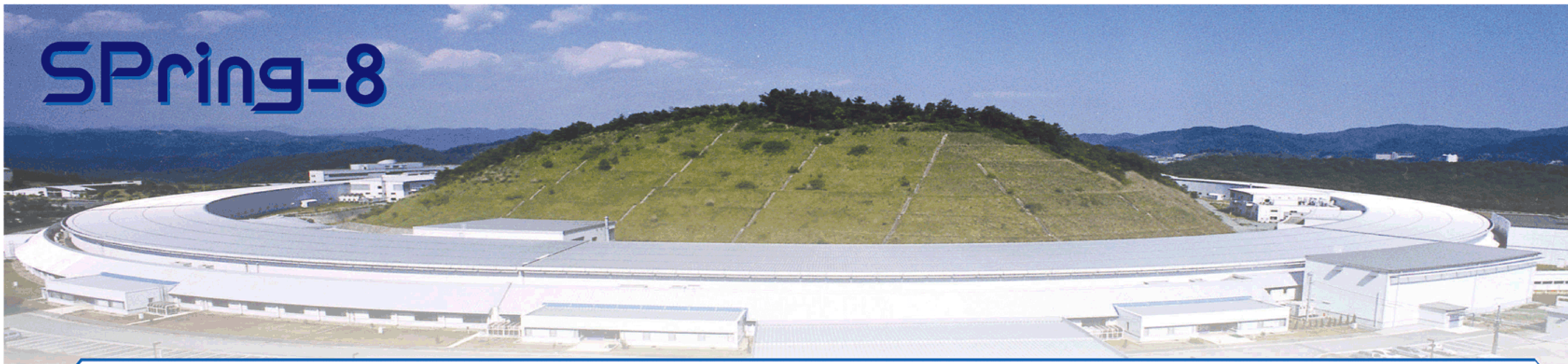

Discovery of a New Material That Shrinks upon Heating

A research group led by Masaki Azuma (formally an associate professor at the Institute for Chemical Research, Kyoto University; currently a professor at the Materials and Structures Laboratory, Tokyo Institute of Technology), Yuichi Shimakawa (a professor at the Institute for Chemical Research, Kyoto University), Masaichiro Mizumaki (an associate senior scientist of the Japan Synchrotron Radiation Research Institute (JASRI)), and Tetsu Watanuki (an associate senior scientist of Japan Atomic Energy Agency) has discovered an oxide material $Bi_{0.95}La_{0.05}NiO_3$ that undergoes colossal negative thermal expansion, at least threefold that of previously reported materials, near room temperature. $Bi_{0.95}La_{0.05}NiO_3$ is obtained by a partial chemical substitution of La for Bi in pure $BiNiO_3$ that shows a pressure induced intermetallic charge transfer between Bi and Ni ions. La substitution for Bi enabled the charge transfer to take place when heated at ambient pressure. The oxidation of Ni ion results in the shrinkage of the framework of the perovskite structure. This discovery was achieved by powder neutron diffraction (PND) studies at the Rutherford Appleton Laboratory, and X-ray absorption spectroscopy (XAS) and powder X-ray diffraction (XRD) studies at SPring-8. The group also found that the temperature range at which negative thermal expansion is observed can be controlled by changing the amount of La substitution for Bi.

Materials with negative thermal expansion are used to compensate the thermal expansion of structural materials when precise positioning is required for optical communication devices and semiconductor manufacturing equipment. It is hoped that the fabrication of zero-expansion materials having high workability and zero expansion and zero shrinkage with changes in temperature will be possible by dispersing a small amount of the new materials into resin.

This research was carried out by the above-mentioned researchers jointly with scientists of The University of Tokyo, Hiroshima University, the University of Edinburgh (UK), and Rutherford Appleton Laboratory (UK). The results of this study were published in *Nature Communications* on 14 June 2011.

Reference: M. Azuma, W.-T. Chen, H. Seki, M. Czapski, S. Olga, K. Oka, M. Mizumaki, T. Watanuki, N. Ishimatsu, N. Kawamura, S. Ishiwata, M. G. Tucker, Y. Shimakawa and J. P. Attfield; *Nature Communications* **2**, 347 (2011)

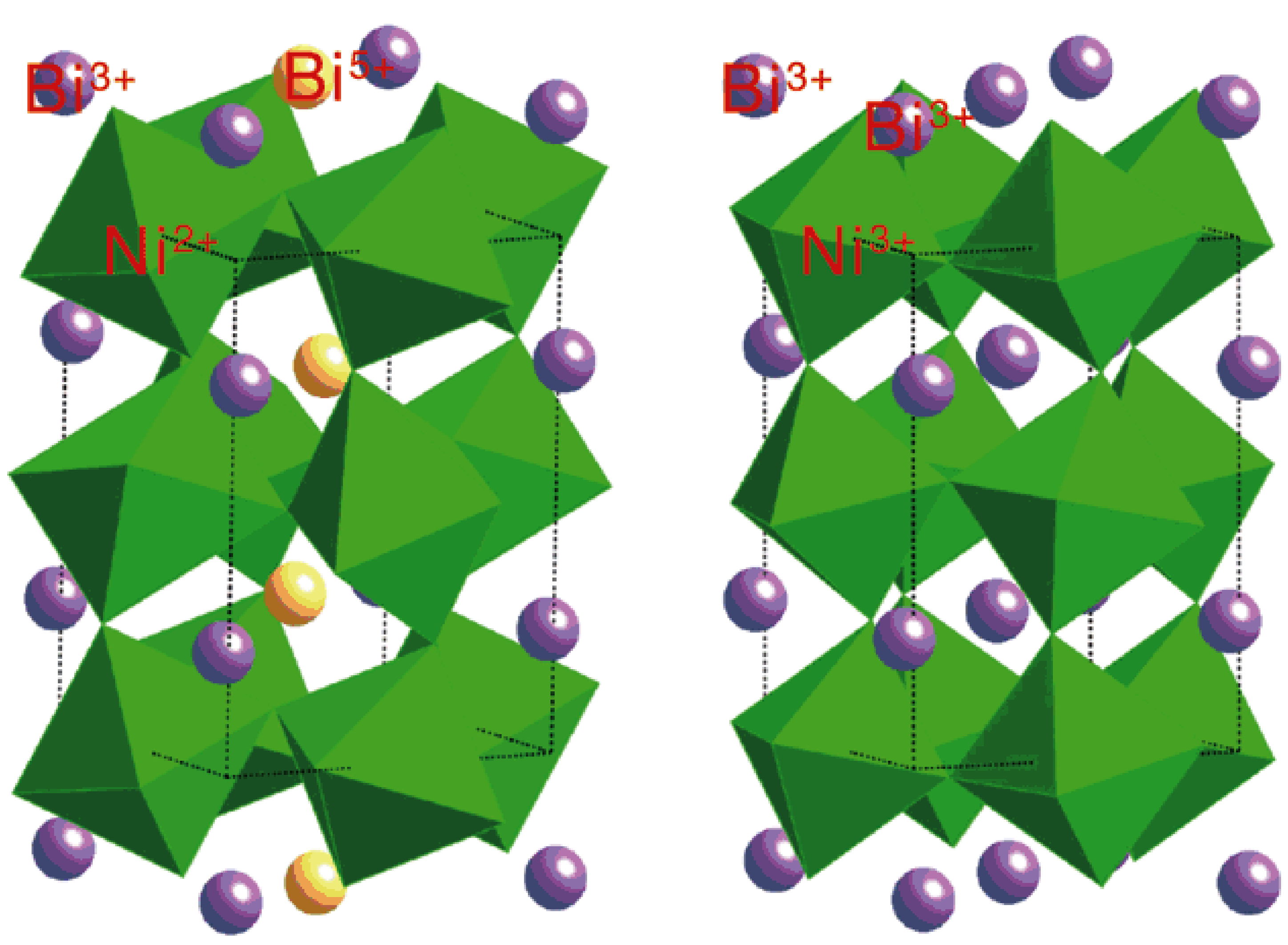

Fig. 1 Crystal structures of $BiNiO_3$ under ambient pressure and temperature(left; $Bi^{3+}_{0.5}Bi^{5+}_{0.5}Ni^{2+}O_3$), and high pressure and temperature (right; $Bi^{3+}Ni^{3+}O_3$)

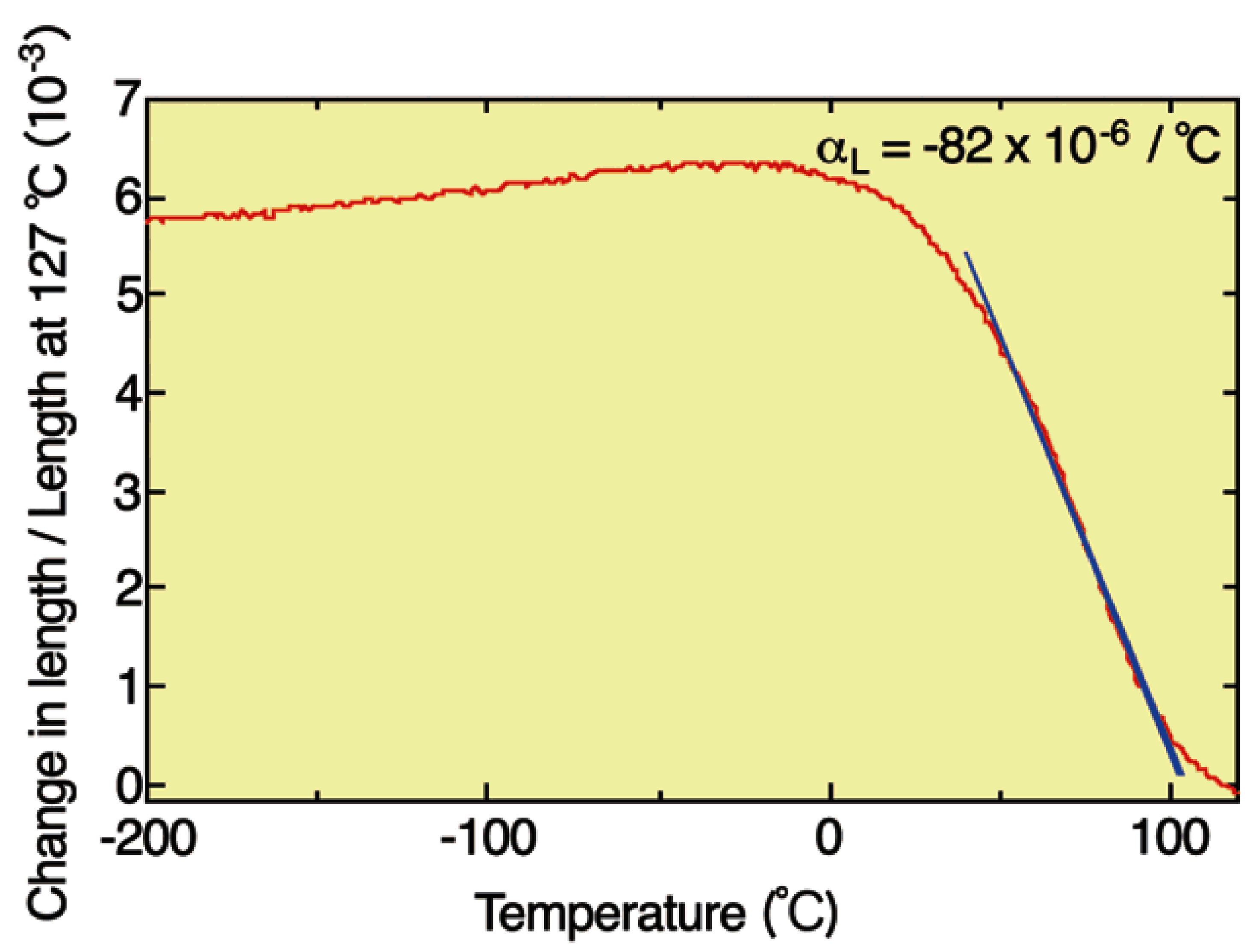

Fig. 2 Change in length of $Bi_{0.95}La_{0.05}NiO_3$ with temperature measured using strain gauge

Negative thermal expansion occurs between 7 and 127 °C, under which the linear thermal expansion coefficient α_L is -82×10^{-6}/°C, at least threefold higher than that of previously reported materials.