

Pressure-induced phase transition in plastic crystal neopentylglycol with colossal barocaloric effects

Caloric effects are phase-transition thermal effects regulated by external fields [1]. In the vicinity of a ferromagnetic-to-paramagnetic transition, an applied magnetic field can effectively suppress the disorder of magnetic moments, which in turn accounts for the entropy changes-this is widely known as the magnetocaloric effect (MCE). Similarly, an electrocaloric effect (ECE) can be also found near a ferroelectric-to-paraelectric transition owing to the alignment of polarizations by electric fields. In some elastically active compounds known as ferroelastics, an external compressive or tensile stress can also modify the crystal structure, bringing out the elastocaloric effect (eCE). Unlike the three aforementioned caloric effects that are observed in ferroics, the barocaloric effect (BCE) is not system-selective and can, in principle, be achieved in any atomic system by applying hydrostatic pressure, because pressure is always factored in the free energy of a system. Caloric materials that exhibit caloric effects can be used for solid-state refrigeration through a designated cooling cycle, which is a promising alternative to the vapor compression cycle that is currently in service.

Very recently, we have discovered that a series of plastic crystals exhibits record large BCEs under very weak pressure [2]. Typical entropy changes, whose magnitude characterizes the caloric effect, are about several hundred $J \cdot kg^{-1} \cdot K^{-1}$, which is 10 times better than those in previous materials, as shown in Fig. 1. Plastic crystals (also termed 'orientation-disordered crystals') are a class of highly disordered solids in which organic molecules (sometimes also inorganic structural blocks) are oriented randomly while their mass centers form highly symmetric lattices, such as the face-centered-cubic (fcc) structure [3]. It is worthwhile to note that the largest entropy change reported is

687 J·kg⁻¹·K⁻¹, exceeding that (~520 J·kg⁻¹·K⁻¹) of the popular liquid refrigerant R134a [4].

Selecting neopentylglycol (NPG) as a model material, we collected the heat flow data using a differential scanning calorimeter (DSC) at 0.1, 15.2, 30.4, 45.0, 71.5 and 91.0 MPa. The phase-transition temperature was defined as the temperature at which the heat flow became maximum. The entropy changes under constant pressure were calculated by integrating the heat flow Q(P,T), after subtracting the baseline. As shown in Fig. 2(a), for a pressure change from ambient pressure to 91.0 MPa, the directly measured entropy change is 384 J kg⁻¹·K⁻¹, which is highly consistent with the value of 389 J·kg⁻¹·K⁻¹estimated using the Clausius-Clapeyron relation (Fig. 1). Actually, more than 50% of the maximum entropy changes are achieved at pressures as low as 15.2 MPa, and the entropy changes tend to be saturated at about 45.0 MPa; such low driving pressures are desirable for real applications. Shown in Fig. 2(b) is the P-Tphase diagram, where there is a thermal hysteresis of about 14 K.

To understand the colossal BCEs of NPG, we conducted a structural study using synchrotron X-ray diffraction (XRD) at SPring-8. The high-resolution XRD patterns obtained at SPring-8 **BL02B2** at a wavelength of 0.9994 Å are plotted in Fig. 3(a). A phase transition is observed to take place at about 313 K, consistent with the thermal measurements (Fig. 2). Rietveld refinement analysis suggests that at room temperature, the NPG molecules are ordered on a monoclinic lattice with space group $P2_1/n$ [5]. This ordered phase transforms into an fcc lattice on heating. The lattice constants are summarized in Fig. 3(b) as a function of temperature. The high-pressure XRD data were collected at **BL04B2** using a diamond anvil cell at a



Fig. 1. Plastic crystals with colossal BCEs for next-generation solid-state refrigeration technology: NPG, pentaglycerin (PG), pentaerythritol (PE), AMP, tris(hydroxymethyl)aminomethane (TRIS), 2-methyl-2-nitro-1-propanol (MNP), 2-nitro-2-methyl-1,3-propanediol (NMP).



Fig. 2. (a) Pressure-induced entropy changes during heating for pressure change from ambient pressure to 15.2, 30.4, 45.0, 71.5 and 91.0 MPa. (b) P-T phase diagram determined using high-pressure DSC.

wavelength of 0.3324 Å. The pressure was determined using a ruby pressure scale. At 318 K, the compound crystallizes in the disordered phase under ambient pressure. Upon applying a pressure of 200 MPa, this phase was converted into the ordered phase, as shown in Fig. 3(c), directly indicating that applying pressure can certainly induce the phase transition.

The discovery of the colossal BCEs in plastic crystals indicates a new direction for caloric materials research. With the help of *in situ* high-pressure XRD, we are able to attribute the observed colossal BCEs to the pressure-induced disorder-to-order transition.



Fig. 3. (a) High-resolution XRD patterns obtained at BL02B2. (b) Lattice constants as a function of temperature. (c) High-pressure XRD patterns at 318 K obtained at BL04B2.

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