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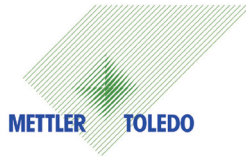
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Conventional and inverse barocaloric effects around triple points in ferroelastics $(\text{NH}_4)_3\text{NbOF}_6$ and $(\text{NH}_4)_3\text{TiOF}_5$

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Barocaloric effect (BCE) associated with the reversible change in the entropy/temperature, $\Delta S_{\text{BCE}}/\Delta T_{\text{AD}}$, under pressure variation under the isothermal/adiabatic conditions is characteristic for substances of different physical origin. The values of extensive, $\Delta S_{\text{BCE}} = -\int (\partial V/\partial T)_p dp$, and intensive, $\Delta T_{\text{AD}} = -\int (T/C_p)(\partial V/\partial T)_p dp$, BCE strongly depend on a coefficient of the volume thermal expansion $\beta = V^{-1}(\partial V/\partial T)_p$. Solids under usual conditions show as a rule rather low β compared to gaseous refrigerants used in the traditional vapor – compression systems. However, near phase transitions the $(\partial V/\partial T)_p$ of solids can often vary by several orders of magnitude. In such a case ΔS_{BCE} and ΔT_{AD} can reach very large magnitudes [1]. Moreover, when heated through a point of the phase transition, the structural distortions may be accompanied by either increase or decrease in the unit cell volume. Thus, BCE can be either conventional, $(\partial V/\partial T)_p > 0$, associated with decrease in ΔS_{BCE} and increase in ΔT_{AD} under applying pressure or inverse, $(\partial V/\partial T)_p < 0$, $\Delta S_{\text{BCE}} > 0$ and $\Delta T_{\text{AD}} < 0$.

In the present work, we investigated barocaloric properties of the two ferroelastic oxyfluorides $(\text{NH}_4)_3\text{NbOF}_6$ and $(\text{NH}_4)_3\text{TiOF}_5$. At ambient pressure, niobate undergoes two structural phase transitions in a very narrow temperature range: $T_1=260$ K and $T_2=262$ K, whereas titanate shows only one phase transition at $T_0=264.7$ K. Entropy of the structural transformations was found very large, in $(\text{NH}_4)_3\text{NbOF}_6$ $\Delta S_1+\Delta S_2=(8.5+30.3)$ J/mol·K and in $(\text{NH}_4)_3\text{TiOF}_5$ $\Delta S_0=18.1$ J/mol·K, and independent on pressure, at least up to 0.5 GPa. The T - p phase diagrams show triple points and crystal phases induced by high pressure.

The dependences of $\Delta T_{\text{AD}}(T,p)$ and $\Delta S_{\text{BCE}}(T,p)$ were determined analyzing data on the heat capacity, the T - p phase diagrams and the dependences of entropy of the phase transitions on temperature and pressure. It was found that the maximum values of the extensive and intensive BCE can be realized at rather low pressure (0.1–0.3 GPa). BCE observed around the triple points demonstrate options worthy of attention and are comparable with the caloric parameters of the known solid refrigerants of different origin [1,2]. In both compounds, the conversion from the conventional BCE to the inverse is observed in very narrow temperature range and followed by gigantic change of both $|\Delta S_{\text{BCE}}|$ and $|\Delta T_{\text{AD}}|$.

The possibility of improving the barocaloric properties by changing the chemical pressure is discussed.

Acknowledgements

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2. Mañosa L, Planes A. Materials with giant mechanocaloric effects: cooling by strength. *Adv Mater.* 2017;29:1603607.

CONVENTIONAL AND INVERSE BAROCALORIC EFFECTS AROUND TRIPLE POINTS IN FERROELASTICS $(\text{NH}_4)_3\text{NbOF}_6$ AND $(\text{NH}_4)_3\text{TiOF}_5$

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Introduction

In recent years, much attention is paid to caloric effects (CE) in solids associated with the reversible change in the temperature, ΔT_{AD} , or entropy, ΔS_{CE} , under variation of the external field in adiabatic and isothermal conditions, respectively [1]. This interest is due, in part, to the possibility to use the materials with large CE as solid state refrigerants in alternative cooling cycles [2].

Among CE of different physical nature, the barocaloric effect (BCE) is distinguished by a serious advantage associated with its universality. Indeed, both extensive ΔS_{BCE} and intensive ΔT_{AD} barocaloric parameters strongly depend on the thermal expansion $(\partial V/\partial T)_p$ which very often shows large change near the temperature of any phase transitions: ferroelectric, ferroelastic, ferromagnetic

$$\Delta S_{BCE} = - \int (\partial V/\partial T)_p dp; \quad \Delta T_{AD} = \int (T/C_p)(\partial V/\partial T)_p dp,$$

where C_p is the heat capacity. In accordance with the $(\partial V/\partial T)_p$ behaviour, BCE can be either conventional, $(\partial V/\partial T)_p > 0$, associated with decrease in ΔS_{BCE} and increase in ΔT_{AD} under applying pressure or inverse, $(\partial V/\partial T)_p < 0$, $\Delta S_{BCE} > 0$ and $\Delta T_{AD} < 0$.

Main Objectives

Study of the role of the sensitivity to hydrostatic pressure in the formation of a variety of barocaloric properties in two cubic oxyfluorides, $(\text{NH}_4)_3\text{NbOF}_6$ and $(\text{NH}_4)_3\text{TiOF}_5$, characterized by a significant structural disorder.

Experimental

Compounds under study were obtained from solution. XRD examination showed an absence of the secondary phases and revealed a cubic structure (sp. gr. $Fm\bar{3}m$) at room temperature in both oxyfluorides. The $T-p$ phase diagrams were built using Differential thermal analysis (DTA) under pressure.

Results and Discussion

In accordance with preliminary heat capacity measurements at ambient pressure performed using an adiabatic calorimeter, $(\text{NH}_4)_3\text{NbOF}_6$ and $(\text{NH}_4)_3\text{TiOF}_5$ undergo two $G_0 \leftrightarrow G_1 \leftrightarrow G_2$ and single $G_0 \leftrightarrow G_1$ phase transitions, respectively, at temperatures presented in Table 1.

Table 1: Barocaloric properties of $(\text{NH}_4)_3\text{NbOF}_6$ and $(\text{NH}_4)_3\text{TiOF}_5$ ferroelastics.

Crystal	G_0-G_1	G_1-G_2	G_1-G_1'	$G_1'-G_2$	G_0-G_1	G_0-G_2	G_2-G_1	G_2-G_3	G_1-G_3
T_i (K)	261	260			265				
dT_i/dp (K/GPa)	54	16	16	3	6.3	223	-176	-59	425
ΔS_{BCE} (J/kgK)	-31	-109	-36	-72	-85	-5.0	60	100	-36
ΔT_{AD}^{max} (K)	6.2	21.7	7.2	14.4	15.3	4.4	-11.5	-17.4	7
p_{min} (GPa)	0.11	1.35			2.4	$0.02+p_{tr}$	$0.06+p_{tr}$	$0.29+p_{tr}$	~ 0.01

Very large entropy change, $\Delta S = \int (\Delta C_p/T) dT$, associated with transformations was found:

$(\text{NH}_4)_3\text{NbOF}_6$: $\Delta S_1 + \Delta S_2 = (8.5 + 30.3) \text{ J/mol}\cdot\text{K}$,

$(\text{NH}_4)_3\text{TiOF}_5$: $\Delta S_0 = 18.1 \text{ J/mol}\cdot\text{K}$.

Due to the negligible effect of the low pressure ($p \leq 0.5 \text{ GPa}$) on the anomalous entropy, ΔS_i , (Figs. 1(a) left and right), we assume that lattice entropy, S_{LAT} of fluorine-oxygen crystals with dominated ionic bonds also does not substantially depend on the hydrostatic pressure.

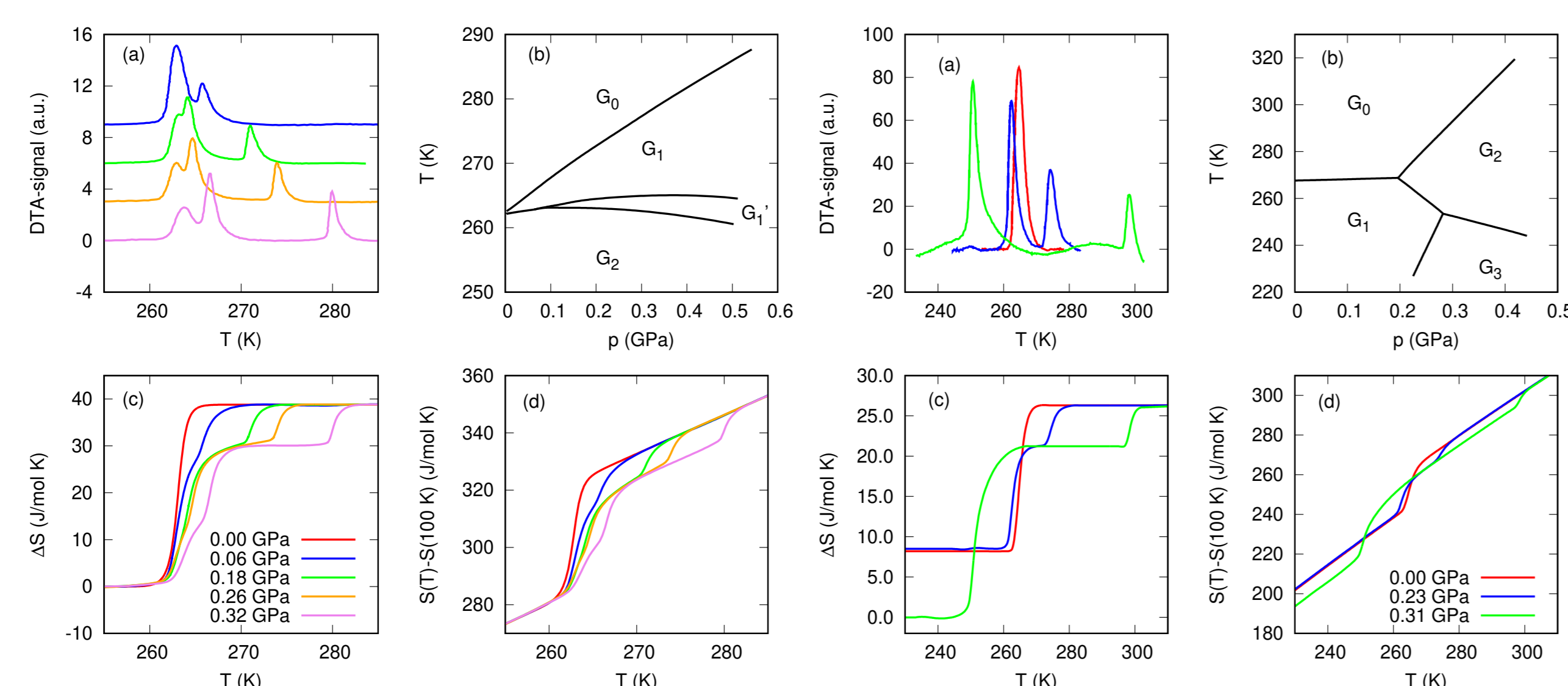


Figure 1: The dependences of (a) DTA-signal and (c) excess entropy ΔS on temperature at different hydrostatic pressure; (b) $T-p$ phase diagram; (d) temperature dependence of total entropy at different hydrostatic pressure for $(\text{NH}_4)_3\text{NbOF}_6$ (left) and $(\text{NH}_4)_3\text{TiOF}_5$ (right).

The main common features:

1. Entropy of the structural transformations does not depend on pressure.
2. Both $T-p$ diagrams demonstrate the triple points initiated by the rather low pressure 0.1–0.3 GPa.
3. Pressure increase leads to the expansion of the temperature range of intermediate phases.

To analyze BCE, temperature dependences of the total entropies under pressure (Figs. 1(d) left and right) were determined as a sum of S_{LAT} and ΔS_i shifted along the temperature scale according to the appropriate sign and value of the baric coefficient dT_i/dp (Table 1).

Extensive and intensive barocaloric parameters were determined as $\Delta S_{BCE} = S(T, p) - S(T, p = 0)$ and $S(T, p) = S(T + \Delta T_{AD}, p = 0)$.

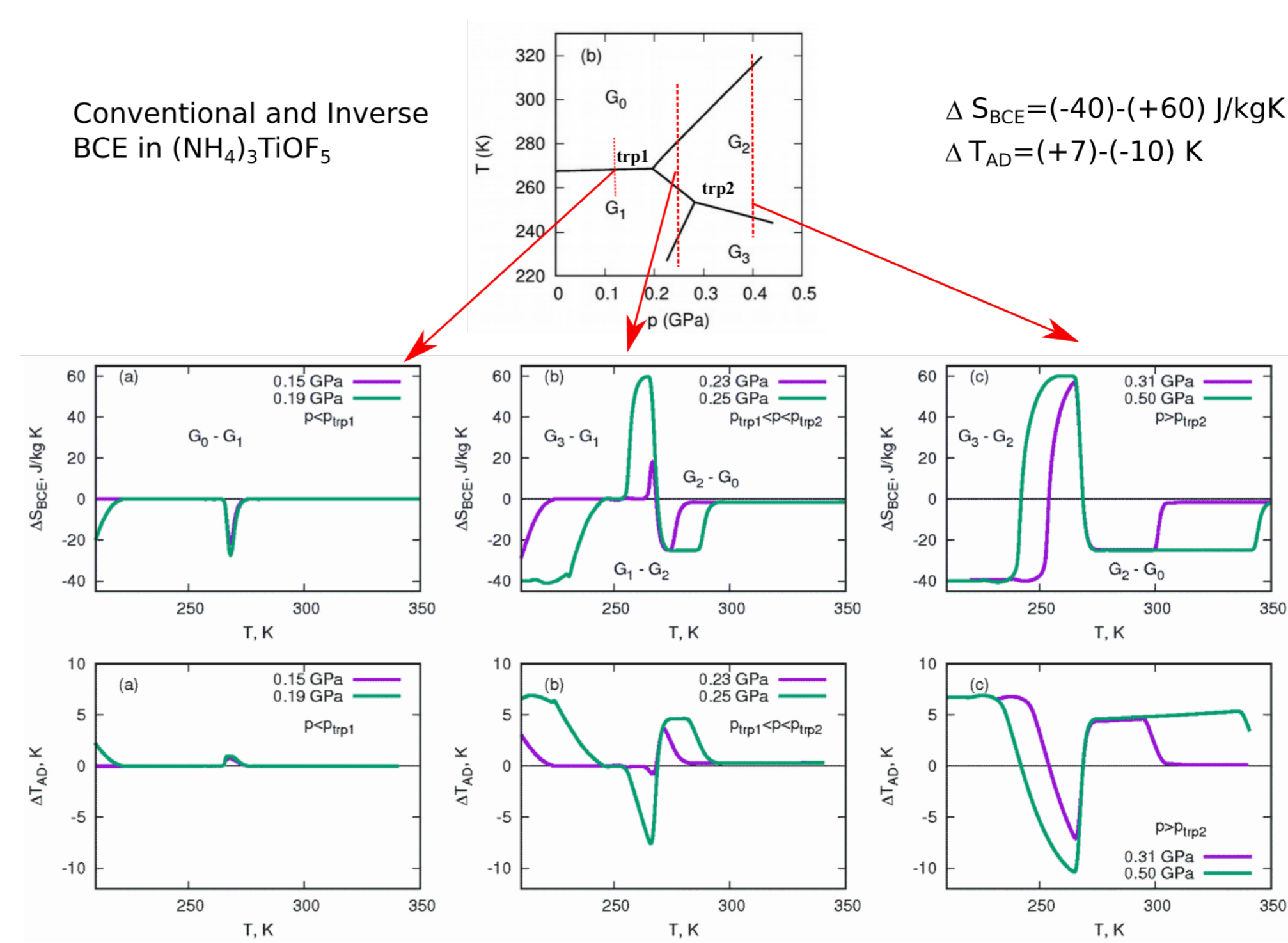


Figure 2: Successive transformation of BCE in $(\text{NH}_4)_3\text{TiOF}_5$ with increasing pressure.

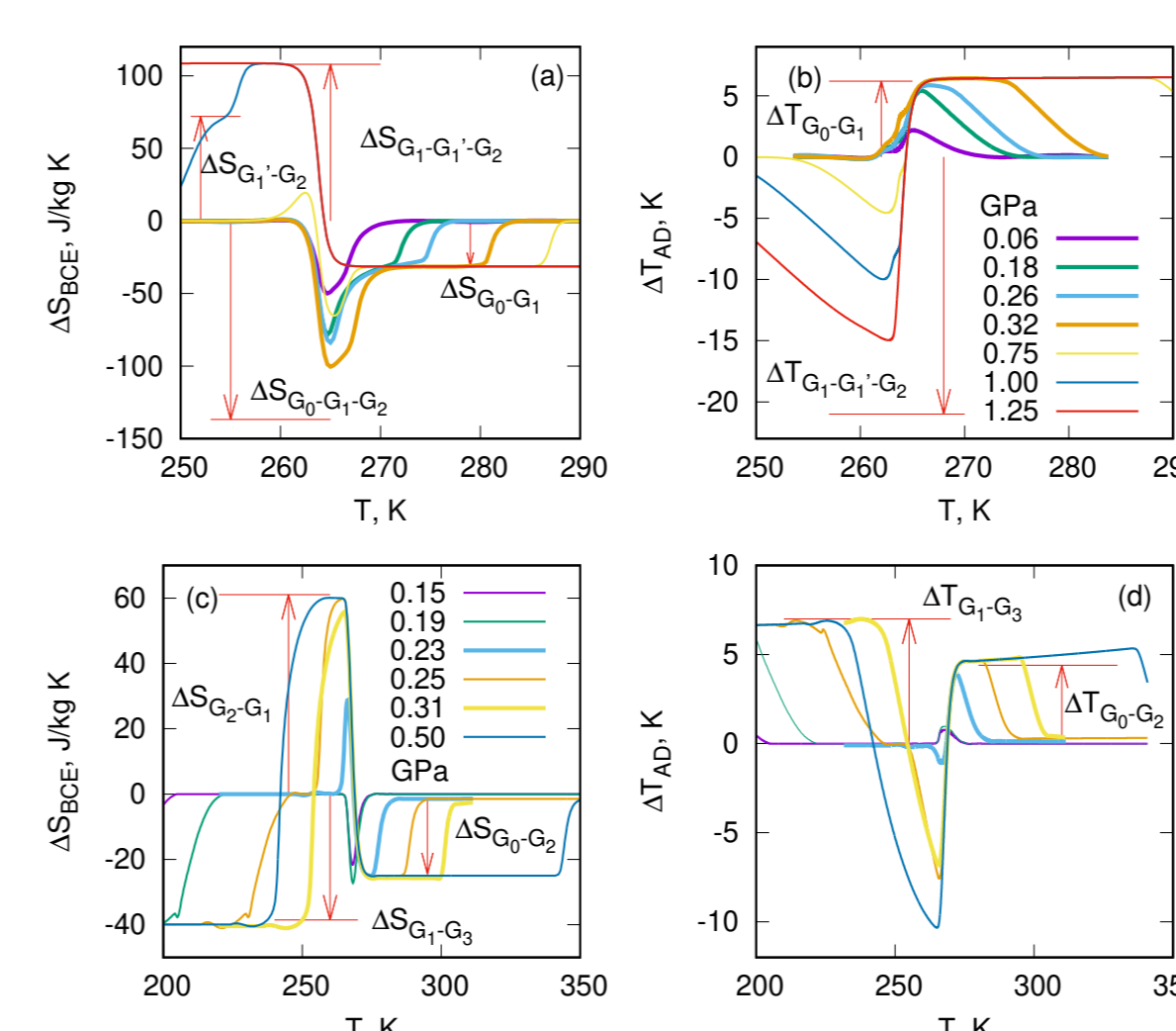


Figure 3: Temperature dependences of barocaloric entropy and temperature changes at different hydrostatic pressure: (a, b) in $(\text{NH}_4)_3\text{NbOF}_6$ and (c, d) in $(\text{NH}_4)_3\text{TiOF}_5$.

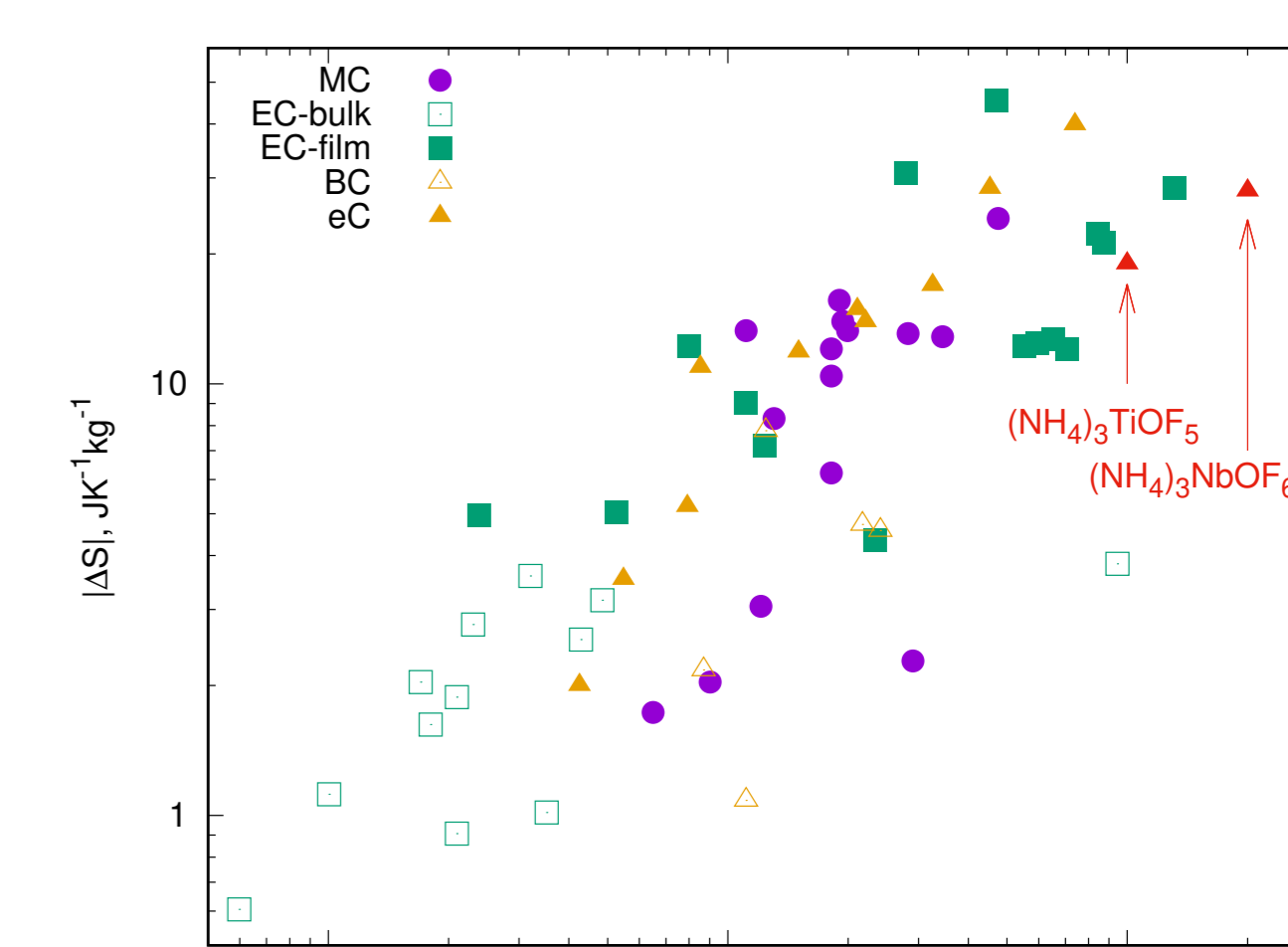


Figure 4: Comparison of combinations of intensive and extensive effects in materials of different physical nature. (MC—magnetocaloric effect; EC—electrocaloric effect; eC—elastocaloric effect; BC—barocaloric effect).

One more important parameter of the barocaloric efficiency considered as a minimum pressure, $p_{min} = T\Delta S/(C_{LAT}dT/dp)$, required to implement maximum BCE was found very low for some phase transitions in both oxyfluorides (Table 1).

Conclusions

1. A very important point is that, contrary to some ferroelectric crystals rather low hydrostatic pressure has practically no effect on entropy of ferroelastic transformations, therefore the behavior of extensive and intensive BCE is not changed with increase in pressure.
2. In both compounds, relatively low pressure 0.01–0.60 GPa can initiate:
 - a) the conversion from the conventional BCE to the opposite and vice versa which is observed in very narrow temperature range;
 - b) gigantic change in both BCE $|\Delta S_{BCE}| = 30-100 \text{ J/kgK}$; $|\Delta T_{AD}| = 4-22 \text{ K}$, which are comparable with the caloric parameters of the known solid refrigerants of different origin (Fig. 4).
3. In the case of $(\text{NH}_4)_3\text{TiOF}_5$, it is safe to assume that by increasing the chemical pressure, for example by cationic substitution, one can move both triple points to the area of significantly lower external pressure.

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1. Moya X, Kar-Narayan S, Mathur ND. Caloric materials near ferroic phase transitions. *Nat Mater.* 2014;**13**:439–50.
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