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To cite this article: E. A. Mikhaleva , I. N. Flerov , V. S. Bondarev , M. V. Gorev , A. D. Vasiliev & T. N. Davydova (2012) Electrocaloric and Barocaloric Effects in Some Ferroelectric Hydrosulfates and Triglycinesulfate, *Ferroelectrics*, 430:1, 78-83, DOI: [10.1080/00150193.2012.677717](https://doi.org/10.1080/00150193.2012.677717)

To link to this article: <https://doi.org/10.1080/00150193.2012.677717>



Published online: 14 Jun 2012.



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# Electrocaloric and Barocaloric Effects in Some Ferroelectric Hydrosulfates and Triglycinesulfate

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*A comparative analysis of electrocaloric and barocaloric efficiency of order-disorder ferroelectrics  $Rb_x(NH_4)_{1-x}HSO_4$  and TGS is performed. A good agreement was found between intensive electrocaloric effects measured experimentally and calculated using electric equation of state. Barocaloric effects were evaluated analyzing the experimental data on heat capacity and T-p phase diagrams. In some crystals under study the same adiabatic temperature change can be produced by low pressure and rather high electric field.*

**Keywords** Ferroelectrics; phase transitions; electrocaloric and barocaloric effects

**PACS:** 65.40.-b; 77.70.+a; 77.80.Bh

## Introduction

Electro (ECE)-, magneto (MCE)- and baro (BCE)-caloric effects in solids can be realized by two ways under external field of corresponding physical nature. The adiabatic field change leads to the temperature variation known as intensive caloric effect  $\Delta T_{AD}$ . A reversible entropy change  $\Delta S^{CE}$  resulted from the field variation at constant temperature and characterized by the opposite sign compared to  $\Delta T_{AD}$  associates with the extensive caloric effect.

In recent years, a giant caloric response found in some ferromagnets [1] and ferroelectrics [2] has stimulated both basic and applied interests in the development of materials that are useful for magnetic-electric refrigeration. In regard to BCE, it has not been studied in solids so widely and intensively as ECE and MCE. However this property is very attractive because of its generality for materials of any physical nature (ferroelectric, ferromagnetic, ferroelastic, etc.). Really, in accordance with the Maxwell's relation

$$(\partial S / \partial p)_{T, E, H} = -(\partial V / \partial T)_{p, E, H}, \quad (1)$$

where p, E, H are hydrostatic pressure, electric and magnetic fields, respectively, the magnitude of extensive BCE  $\Delta S^{BCE}$  depends on the temperature derivative of volume deformation which is known to be the largest usually near phase transition point.

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Received June 26, 2011; in final form November 30, 2011.

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Of particular interest is the study of the feasibility of different caloric effects in the same material. First, this allows us to get more information about the nature and mechanism of phase transitions. Second, simultaneous using distinct external fields can increase the total caloric efficiency of the material. Only a few studies are known to be devoted to BCE and MCE in the same magnetic material [3]. As to the ferroelectrics, up to now, their barocaloric efficiency was not studied.

In this work, we analyze ECE and BCE in the series of crystals  $\text{Rb}_x(\text{NH}_4)_{1-x}\text{HSO}_4$  undergoing depending on  $x$  the successions of order-disorder phase transitions  $P2_1/c \rightarrow Pc \rightarrow P-1$  ( $x = 0, 0.02, 0.04$ ) and  $P2_1/c \rightarrow Pc$  ( $x = 0.33, 1$ ) [4–6]. It was also intriguing to evaluate BCE to compare it with ECE in hydrosulfates as well as in triglycinesulfate (TGS) characterized by rather large value of phase transition entropy  $\Delta S = 6.8 \text{ J/mol}\cdot\text{K}$  [7] in comparison with  $\text{Rb}_x(\text{NH}_4)_{1-x}\text{HSO}_4$  compounds ( $\Delta S \leq 1.7 \text{ J/mol}\cdot\text{K}$ ) [4–6].

## Discussion

For the aims above we analyzed the experimental data on heat capacity, permittivity, intensive ECE and baric coefficients for  $\text{Rb}_x(\text{NH}_4)_{1-x}\text{HSO}_4$  [4–6, 8, 9] and TGS [7, 10–12].

First of all we considered the excess heat capacity  $\Delta C_p(T)$  in the framework of Landau thermodynamic theory. In accordance with [13] from the thermodynamic potential for the second order phase transitions

$$\Delta \Phi = A_T(T - T_{PT})P^2 + BP^4 + CP^6 - EP \quad (2)$$

at  $E = 0$  one can derive equation

$$\left(\frac{\Delta C_p}{T}\right)^{-2} = \left(\frac{2\sqrt{B^2 - 3A_T C}}{A_T^2}\right)^2 + \frac{12C}{A_T^3}(T_{PT} - T) \quad (3)$$

It was found that in all crystals under study,  $(\Delta C_p / T)^{-2}(T)$  is a linear function in rather wide temperature range  $\Delta T_L$  below the phase transition point  $T_{PT}$  (Table 1). Using the permittivity data we have evaluated the values of coefficients in (2) (Table 1). One can see that even rather small addition of rubidium ( $x = 0.33$ ) in  $\text{Rb}_x(\text{NH}_4)_{1-x}\text{HSO}_4$  solid solutions leads to decrease of  $\Delta T_L$  and to increase of  $N = (B^2/3A_T \cdot C \cdot T_{PT})^{\frac{1}{2}}$  value, which characterizes a closeness of phase transition to tricritical point.

**Table 1**

Phase transition temperature  $T_{PT}$ ; temperature range  $\Delta T_L$  associated with equation (3); coefficients  $A_T$ ,  $B$ ,  $C$  of thermodynamic potential (2); closeness to the tricritical point  $N$

Crystal	$T_{PT}$ , K	$\Delta T_L$ , K	$A_T \cdot 10^2$ , $\text{K}^{-1}$	$B$ , $(\text{J/mol})^{-1}$	$C$ , $(\text{J/mol})^{-2}$	$N$
$\text{NH}_4\text{HSO}_4$	271.7	190–271.7	3.0	$8.9 \cdot 10^{-3}$	$2.3 \cdot 10^{-4}$	0.12
$\text{Rb}_{0.33}(\text{NH}_4)_{0.67}\text{HSO}_4$	269	220–265	1.4	$4.0 \cdot 10^{-3}$	$2.5 \cdot 10^{-5}$	0.24
$\text{RbHSO}_4$	264.6	240–262	5.0	0.04	$8.4 \cdot 10^{-4}$	0.22
TGS	322.3	310–321	0.18	$5.7 \cdot 10^{-6}$	$1.4 \cdot 10^{-9}$	0.12

Taking into account a small effect of electric field on the coefficient  $A_T$  [12] an analysis of the electric equation of state  $\partial\Delta\Phi/\partial P = 0$  was performed and the polarization – temperature – electric field (P–T–E) surfaces were built. By analogy with equation (1) one can write Maxwell's relation for ferroelectrics

$$\left(\frac{\partial S}{\partial E}\right)_{P,T} = \left(\frac{\partial P}{\partial T}\right)_{P,E}. \quad (4)$$

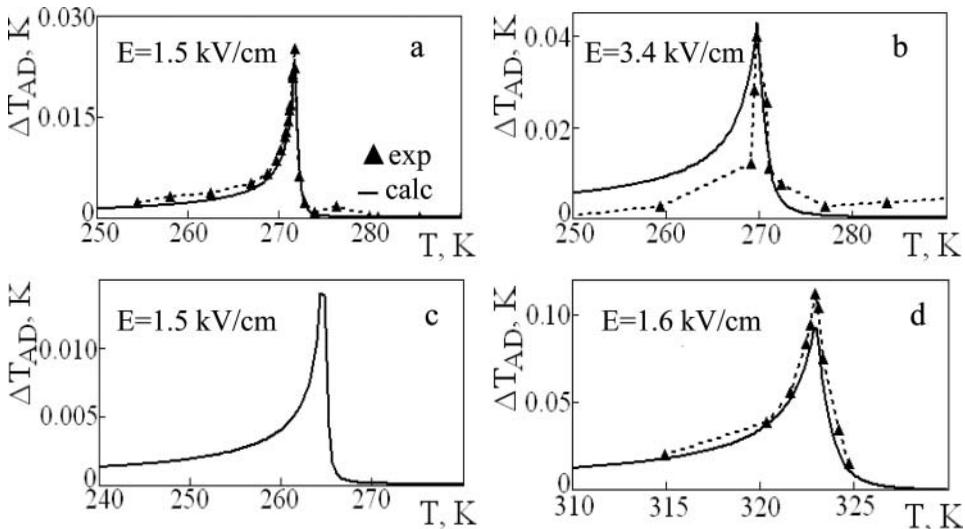
Hence it follows that intensive electrocaloric effect can be expressed as

$$dT_{AD}^{ECE} = -(T/C_{p,E})(\partial P/\partial T)_{p,E}dE. \quad (5)$$

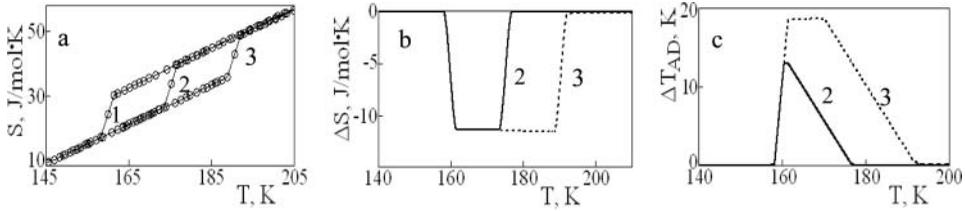
Using the results of consideration of the electric equation of state the values of  $\Delta T_{AD}^{ECE}$  were determined for solid solutions  $Rb_x(NH_4)_{1-x}HSO_4$  ( $x = 0, 0.33, 1$ ) as well as for TGS crystal at electric fields used in experiments [4, 10]. Satisfactory agreement between evaluated and experimentally found values as well as their temperature dependences was found for all crystals under investigation (Fig. 1). The maximum magnitudes of  $\Delta T_{AD}^{ECE}$  in solid solutions differ from each other (at the same E) in accordance with N value because the temperature derivative of polarization increases with N decrease. Thus, the results obtained prove the potentialities of the considered in present paper method of indirect determination of  $\Delta T_{AD}^{ECE}$  on the ground of heat capacity and permittivity investigations.

The most reliable way to determine caloric effects is to perform the direct measurements of temperature change by means, for example, of adiabatic calorimeter. Really this way is relatively simple for the study of ECE and MCE [3, 4, 10]. But for the barocaloric measurements this method is not convenient. This is the reason that investigators try often to obtain information concerning barocaloric parameters analyzing the experimental data obtained by other experimental techniques. We have evaluated barocaloric efficiency of crystals under study in the framework of approaches developed in [14].

Destruction of the  $NH_4HSO_4$  single crystal at strong first order phase transition  $P_c \rightarrow P_1$  at  $T_2$  prevents the studying of ECE. On the other hand, rather large changes of entropy



**Figure 1.** Experimentally measured and calculated intensive ECE  $\Delta T_{AD}$  for  $NH_4HSO_4$  (a),  $Rb_{0.33}(NH_4)_{0.67}HSO_4$  (b),  $RbHSO_4$  (c) and TGS (d).

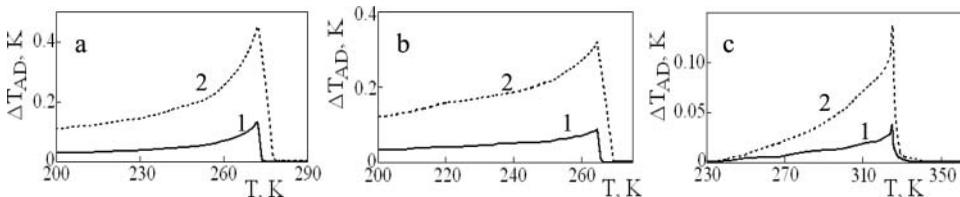


**Figure 2.** Total entropy  $S$  (a), extensive  $\Delta S$  (b) and intensive  $\Delta T_{AD}$  (c) BCE for  $\text{NH}_4\text{HSO}_4$  in the vicinity of  $Pc \rightarrow P-I$  phase transition;  $p = 0$  bar (1);  $p = 200$  bar (2);  $p = 400$  bar (3).

$\Delta S_2 = 1.4R$  and volume  $\Delta V_2/V \approx 1.2\%$  as well as giant baric coefficient  $dT_2/dp = 76.5$  K/kbar make this transformation very promising for examination of BCE.

One can assume that there is a negligible small effect of rather low pressure ( $p < 10$  kbar) on lattice heat capacity  $C_L$  and lattice entropy  $S_L$ . Hence the total entropy  $S(p, T)$  at  $p > 0$  can be determined as the sum of pressure independent  $S_L = \int (C_p/T) dT$  part and anomalous  $\Delta S_2 = \int (\Delta C_p/T) dT$  contribution determined at  $p = 0$  and shifted along temperature scale at  $p > 0$  in accordance with  $dT_2/dp$  value [1]. In Fig. 2(a) the total entropy is shown versus temperature for several pressures. The values of extensive BCE were evaluated as the difference  $\Delta S^{\text{BCE}}(T, p) = S(T, p \neq 0) - S(T, p = 0)$  at constant temperature (Fig. 2(b)). Evidently saturated value of  $\Delta S^{\text{BCE}}$  will be equal to the entropy of phase transition  $Pc \rightarrow P-I$ , which is rather large  $\sim R \ln 4$  in  $\text{NH}_4\text{HSO}_4$  at  $T_2$  [5]. The intensive BCE  $\Delta T_{AD}^{\text{BCE}}$  was determined as the temperature change at constant entropy depending on pressure (Fig. 2(c)). The maximum value  $\Delta T_{AD}^{\text{BCE}} \approx 19$  K is comparable with those in ferromagnetic and ferroelectric materials considered as promising solid refrigerants [1, 2]. It is of first importance that the pressure needed to realize the maximum BCE at  $T_2$  in  $\text{NH}_4\text{HSO}_4$  is relatively low  $p \geq 0.3$  kbar.

Using the procedure above the adiabatic temperature change with pressure variation was determined in the vicinity of the second order phase transitions in  $\text{Rb}_x(\text{NH}_4)_{1-x}\text{HSO}_4$  and TGS. Because of low entropies ( $\Delta S < \ln 2$ ) the  $\Delta T_{AD}^{\text{BCE}}$  quantities also appear to be insignificant (Fig. 3). It is seen that  $\text{Rb} \rightarrow \text{NH}_4$  substitution leads to strong decrease of  $\Delta T_{AD}^{\text{BCE}}$  value. The lowest intensive BCE is characteristic for TGS and associates with the lowest baric coefficient  $dT/dp = 2.6$  K/kbar. In Table 2 ECE and BCE are compared. To realize close values of both effects near  $P2_1/c \rightarrow Pc$  transition in  $\text{NH}_4\text{HSO}_4$  very low pressure and high electric field are needed. Comparison of the data obtained shows also that, on the one hand, ECE is the largest in TGS and, on the other, hydrogen sulfate is characterized by the highest barocaloric efficiency thanks to large baric coefficient  $dT_1/dp = 14$  K/kbar.



**Figure 3.** Intensive  $\Delta T_{AD}$  BCE near second order phase transitions in  $\text{NH}_4\text{HSO}_4$  (a),  $\text{RbHSO}_4$  (b) and TGS (c);  $p = 100$  bar (1),  $p = 400$  bar (2).

**Table 2**

Phase transition temperature  $T_{PT}$ , electric field  $E$ , hydrostatic pressure  $p$ , intensive and extensive ECE ( $\Delta T_{AD}^{ECE}$ ,  $\Delta S^{ECE}$ ) and BCE ( $\Delta T_{AD}^{BCE}$ ,  $\Delta S^{BCE}$ ). Data on  $\Delta T_{AD}^{ECE}$  in TGS [10]

Crystal	$T_{PT}$ , K	$E$ , kV/cm	$\Delta T_{AD}^{ECE}$ , K	$\Delta S^{ECE}$ , J/kg·K	$p$ , bar	$\Delta T_{AD}^{BCE}$ , K	$\Delta S^{BCE}$ , J/kg·K
NH <sub>4</sub> HSO <sub>4</sub>	271.7	1.5	0.025	−0.11	20	0.027	−0.12
	160				20	1.3	−57.6
Rb <sub>0.33</sub> (NH <sub>4</sub> ) <sub>0.67</sub> HSO <sub>4</sub>	269	1.5	0.025	−0.076			
RbHSO <sub>4</sub>	264.6	1.5	0.014	−0.044	20	0.02	−0.042
TGS	323	1.6	0.112	−0.617	20	0.007	−0.044

## Conclusions

It is shown that analyzing experimental data about heat capacity and permittivity one can obtain reliable information concerning electrocaloric effects in ferroelectrics undergoing second order phase transitions close to the tricritical point. Ferroelectrics characterized by rather low phase transition entropy and high susceptibility to hydrostatic pressure may show significant barocaloric efficiency compared to electrocaloric one.

## Acknowledgments

This work was supported by the Council on Grants from the President of the Russian Federation for Support of Leading Scientific Schools (project no, Nsh – 4645.2010.2).

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