

Phenomenological Material Model for First-Order Electrocaloric Material

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Abstract: Caloric cooling systems are potentially more efficient than systems based on vapour compression. Electrocaloric cooling systems use a phase transformation from the paraelectric to the ferroelectric state by applying or removing an electric field to pump heat. Lead scandium tantalate (PST) materials show a first-order phase transition and are one of the most promising candidates for electrocaloric cooling. To model caloric cooling systems, accurate and thermodynamically consistent material models are required. In this study, we use a phenomenological model based on an analytical equation for the specific heat capacity to describe the material behaviour of bulk PST material. This model is fitted to the experimental data, showing a very good agreement. Based on this model, essential material properties such as the adiabatic temperature change and isothermal entropy change of this material can be calculated.

Keywords: electrocaloric cooling; electrocaloric material; system simulation; material model; first-order material



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1. Introduction

By 2050, it is projected that more than 95% of the world population will be in need of space cooling due to an average increase in temperature. It is predicted that the electricity demand for air conditioning will rise between 75 and 160%, depending on the scenario [1]. In 2013, more than 99% of air cooling was based on compression systems [2]. Systems based on vapour compression work with harmful refrigerants that often have a high global warming potential as well [3]. However, working with these refrigerants gets more and more regulated [4], so that there is a high need for alternative cooling technologies. Solid-state cooling based on the caloric effect is one of the most promising technologies to replace compressor-based technologies, as it is potentially more efficient [2,5,6]. The typical Carnot efficiency of superior compressor systems is around 50% [7]. In 2018, Chaudron et al. published a magnetocaloric cooling system with an efficiency of 60% [8].

Caloric materials generate a temperature change due to a first- or second-order reversible phase transition [9]. In the case of most electrocalorics, the phase change occurs from the paraelectric to the ferroelectric state (or vice versa) and results from applying or removing an electric field. By cycling the electric field and directing heat towards and from the material, an electrocaloric heat pump can be realised, as, for instance, shown in an electrocaloric regenerator system by Torello et al. [10] or a cascaded system by Wang et al. [11].

For the development and optimisation of caloric cooling systems, it is essential to develop simulation models describing the system behaviour and efficiency, as can be seen in example [12]. However, for proper predictions, these system models depend strongly

on models of the caloric material. One possible way to model caloric materials is via the generalised Maxwell relation

$$\left(\frac{\partial s}{\partial F}\right)_T = \left(\frac{\partial X}{\partial T}\right)_F, \quad (1)$$

wherein s is the specific entropy, F is the field parameter (e.g., the electric field for electrocalorics), T is the temperature and X is the order parameter (e.g., the polarisation). Bonnot et al. [13], Grácia-Condal et al. [14], Pataky et al. [15] and Xiao et al. [16] published elastocaloric materials modeled via this approach. In many cases, the adiabatic temperature change modeled with these equations tend to be overestimated [15–18]. In magnetocalorics, Franko et al. and Lei et al. used a master curve for the isothermal entropy change to model magnetocaloric materials [19,20]. In the case of electrocalorics, Gao et al. used phase field modeling to describe the characteristics of electrocaloric materials [21]. This is a density-based computational technique using the Landau–Devonshire thermodynamic theory of ferroelectrics. Gong et al. compared this approach with the application of the Curie–Weiss law and a Gaussian fit approach [22].

A simple model based on a Cauchy–Lorentz function describing the specific heat capacity of magnetocaloric materials was developed by Hess et al. [23]. In a thermodynamically consistent manner, the isothermal entropy change and the adiabatic temperature change were derived from this equation. Hess et al. developed this model further by taking hysteresis into account as well [24]. Bachmann et al. refined this approach for elastocaloric materials so that dissipative losses and incomplete phase changes were also taken into account [25]. These material models can also be used for determining efficiencies, figure of merits (FOM) and coefficients of performance (COP) of the materials [24]. The biggest advantage in these models for magneto- and elastocalorics is the simplicity of the main equation, especially with regard to the agreement with the measurement data as well. Compared to other known methods as, for example, the quasi-direct method (as seen in Moya et al. [26]), with the phenomenological model, one is able to extract five key material parameters directly from the measurement data. This enables a complete field- and temperature-dependent description of the material's behaviour.

In this paper, we use the material model based on Hess et al. and Bachmann et al. [23–25] to describe the behaviour of electrocaloric lead scandium tantalate (PST) bulk material, as published by Nouchokgwe et al. [27]. We show that the material model that was originally developed for magnetocaloric and developed further for elastocaloric materials describes the behaviour of electrocaloric materials with a very good agreement. We show that hereby it is possible to give a complete description of the temperature- and field-dependent behaviour of the electrocaloric material using only five parameters. In conclusion, with the assumption of a Cauchy–Lorentz function as the main equation for the specific heat capacity, it is possible to model measurement data of different physical quantities of three kinds of calorics with one basic assumption. Another positive aspect of the proposed model is the simple computational implementation as well.

2. Methods and Material

2.1. Methods

As stated in the introduction, the electrocaloric material model used in this work is based on the phenomenological models by Hess et al. [23] and Bachmann et al. [25]. The equation of the specific heat capacity $c_p(T, E)$ is based on a Cauchy–Lorentz function

$$c_p(T, E) = \frac{\Delta s_{\text{iso}}^{\text{max}}}{\pi} \frac{\sigma T}{\sigma^2 + [T - \beta E - T_0]^2} + c_0, \quad (2)$$

as introduced in [25]. In Equation (2), T represents the temperature of the material, $\Delta s_{\text{iso}}^{\text{max}}$ represents the maximum isothermal entropy change, σ represents the half width at half maximum of the curve, T_0 is the peak temperature, E is the electric field strength and β is the

shift of the curve after the field is applied and represents the inverse Clausius–Clapeyron coefficient. Lastly, c_0 describes the heat capacity far from the peak.

For adiabatical application or removal of the electric field, the (specific) entropy s stays constant, i.e.,

$$s(T, 0) = s(T + \Delta T_{\text{ad,rev}}, E), \quad (3)$$

where $\Delta T_{\text{ad,rev}}$ is the adiabatic temperature change of the material. This specific entropy can be calculated by integrating the specific heat capacity [25]

$$s(T, E) = \int_{T_{\text{start}}}^T \frac{c_p(T', E)}{T'} dT', \quad (4)$$

wherein T_{start} represents an auxiliary variable ($T_{\text{start}} \ll T_0$). Using Equations (2)–(4), this results in a recursive expression for the reversible, adiabatic temperature change [25]

$$\begin{aligned} \Delta T_{\text{ad,rev}}(T, E) &= -T + T \exp \left\{ \frac{\Delta s_{\text{iso}}^{\text{max}}}{c_0 \pi} \left(\arctan \left[\frac{T - T_0}{\sigma} \right] - \arctan \left[\frac{T_{\text{start}} - T_0}{\sigma} \right] \right. \right. \\ &\quad \left. \left. + \arctan \left[\frac{T_{\text{start}} - T_0 - \beta E}{\sigma} \right] - \arctan \left[\frac{T + \Delta T_{\text{ad,rev}} - \beta E - T_0}{\sigma} \right] \right) \right\}. \end{aligned} \quad (5)$$

The model is fitted simultaneously to the experimental data of the specific heat capacity and the adiabatic temperature change for various electric fields. A least squares method approach is used, and the experimental data is weighted with the inverse of the product of the maximum value of the data set and the number of data points in this data set. The uncertainties of the model parameters are given by the 95% confidence interval.

2.2. Material

As already stated in the introduction, data from Nouchokgwe et al. [27] was used to model the specific heat capacity and the adiabatic temperature change. Lead scandium tantalate $\text{Pb}(\text{Sc}_{1/2}\text{Ta}_{1/2})\text{O}_3$ (PST) in bulk form was used during the experiments. The specific heat capacity was calculated via the heat flow measured in differential scanning calorimetry (DSC) measurements at isofields. The adiabatic temperature change was measured with an infrared camera at sample temperatures between 283 K to 323 K. A more detailed description of the set ups and the measurements can be found in [27].

3. Results and Discussion

The experimental and modelled data can be found in Figure 1. Figure 1a depicts the specific heat capacity plotted against the temperature, whereas Figure 1b shows the adiabatic temperature change versus the sample temperature T_s . Solid lines represent the model; the dots represent the experimental data. The final result for the model parameters and their errors (corresponding to the 95% confidence intervals) can be found in Table 1. In Figure 1a, only the heating curve of the DSC measurement is displayed. Although the cooling curve was shown in [27] as well, it can be seen that the cooling curve shows a non-constant inverse Clausius–Clapeyron coefficient. Since β is constant at different temperatures in the model, only the heating curve is used for the determination of the model parameters in this case.

Furthermore, there is an offset between the absolute temperature of the specific heat capacity and the adiabatic temperature change data. This is due to the fact that the temperature measurements of the specific heat capacity and the adiabatic temperature change were not performed with the same temperature sensor. Another source for this offset can arise through the heating rates of the DSC measurements. In the literature, it is found that for larger heating rates of the DSC measurements, the peaks shift to larger temperatures [28]. This effect can account for a temperature shift of the peak temperature

to larger temperatures by up to 3 K. It was found that both effects account for an offset of the peak temperature of the DSC data of 4.36 K.

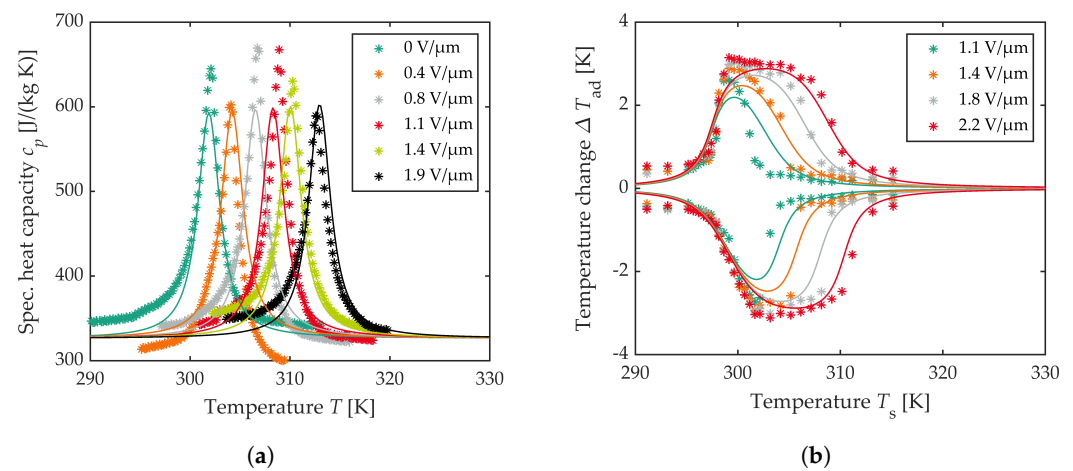


Figure 1. Results after fitting the model to the experimental data. The experimental data is represented by dots; the model is depicted by solid lines. (a) Specific heat capacity versus temperature for various electric field strengths. (b) Adiabatic temperature change versus the sample temperature for various electric field strengths.

Table 1. Model parameters. The error is given by the 95% confidence interval.

Model Parameter	Value $\pm$ Error	Parameter Unit
T_0	(297.51 ± 0.16)	K
$\Delta s_{\text{iso,max}}$	(3.71 ± 0.07)	J/kg/K
c_0	(326.4 ± 1.3)	J/kg/K
σ	(1.34 ± 0.04)	K
β	(5.84 ± 0.03)	K $\mu\text{m}/\text{V}$

As for a more detailed comparison of the model data with the experimental data, the adiabatic temperature change measurements show a slight asymmetry at higher temperatures, which cannot be depicted by the model since the Cauchy–Lorentz function used for the specific heat capacity is a symmetric function. This leads to an overestimation of the adiabatic temperature change at small electric field strengths.

Another issue is the underestimation of the maximum of the specific heat capacity, resulting in a decreased maximum isothermal entropy change.

The heat capacity c_0 at $0.4 \text{ V}/\mu\text{m}$ is smaller than the offsets at larger field strengths. Besides, the experimental data shows an asymmetry in c_0 at high resp. low temperatures, which cannot be displayed in the model.

Overall, the model shows an excellent agreement with the experimental data, especially regarding the simplicity of the model.

4. Conclusions

In this paper, we used a material model that was developed for magnetocaloric [23] and developed further for elastocaloric materials [25] to describe the behaviour of electrocaloric lead scandium tantalate bulk material. We started by using a Cauchy–Lorentz function for the specific heat capacity and used the Maxwell relations to obtain equations for the isothermal entropy change and the adiabatic temperature change. By using only five model parameters (peak width σ , peak temperature T_0 , specific heat capacity c_0 , inverse Clausius–Clapeyron coefficient β and the maximum isothermal entropy change $\Delta s_{\text{iso}}^{\text{max}}$), it is possible to model the field- and temperature-dependent material behaviour of electrocaloric PST. It could be shown that this simple model based on a Cauchy–Lorentz function is in excellent agreement with the measurements of the specific heat capacity and the adiabatic

temperature change at different field strengths. Although the analytical equations were validated with data from bulk PST electrocaloric material, they can be used to describe other electrocaloric materials (e.g., PMN-PT) as well. Moreover, this model can be used for further system simulations of electrocaloric cooling systems. The model can be applied to other electrocaloric material data and can also be extended so that second-order effects can be described.

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Abbreviations

The following abbreviations are used in this manuscript:

COP	Coefficient of Performance
DSC	Differential Scanning Calorimetry
FOM	Figure of Merit
PST	Lead Scandium Tantalate

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