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Heat capacity, thermal expansion and barocaloric effect in fluoride K2TaF7

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Dear Editor,

Consider please our manuscript, devoted to some new results obtained during the study of heat capacity, thermal dilatation and intensive and extensive barocaloric effects near phase transitions in proper ferroelastic K_2TaF_7.

We hope that the results will be of interest to readers of Journal of Materials Science.

Sincerely Yours,

Prof. Igor Flerov

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Heat capacity, thermal expansion and barocaloric effect in fluoride K_2TaF_7

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Abstract Heat capacity and thermal dilatation of potassium heptafluorotantalate were studied. Room temperature phase $P2_1/c$ is stable at least to 4 K. Strong first order phase transition $P2_1/c - Pnma$ at $T_0 = 486.2$ K is accompanied by giant changes in the entropy, $\Delta S_0 = 22.3$ J·(mol·K)$^{-1}$, and volume strain, $\delta V_0/V = -3.6\%$. A rather high sensitivity of K_2TaF_7 to pressure was found, $dT_0/dp = -220$ K G·Pa^{-1}. Significant extensive and intensive barocaloric effects are found at low pressure. The possibility of improving the barocaloric properties is discussed.

Keywords Phase transition · Heat capacity · Entropy · Thermal expansion · Barocaloric effect

Introduction

The shape of the anionic polyhedron in complex inorganic fluorides can be rather different depending on the valency and size of the central atom, and plays an important role in the formation of crystal lattice and physical properties of compounds [1]. Octahedral anions MF_6^{m-} are the most frequent structural building units. However, there are also many compounds with other form of fluorine polyhedron. For example, the structure of fluorides with the general chemical formula A_2MeF_7 consists of the seven-coordinated MeF_7^{2-} anionic complex in the form of mono-capped trigonal prism with C_{2v} symmetry [2]. Heptafluorides A_2TaF_7 (A: K, NH_4, Rb) belonging to this series of crystals are characterized by different room temperature symmetry of the crystal lattice depending on the size of the monovalent cation A. While compounds with A = Rb, NH_4 have tetragonal

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symmetry ($P4/nmm$, $Z = 2$) [3], potassium heptafluorotantalate is monoclinic ($P2_1/c$, $Z = 4$) [2,4]. Crystal lattice stability of heptafluorides with respect to temperature change is also different. The tetragonal phase of the first two crystals is stable when heated to the decomposition temperature. Upon cooling, both compounds undergo unique and successive phase transitions: Rb_2TaF_7 – $P4/nmm$ ($T_0 = 145$ K) – $Cmma$ [5]; $(NH_4)_2TaF_7$ – $P4/nmm$ ($T_1 = 174$ K) – $Pmmn$ ($T_2 = 156$ K) – tetragonal [6]. In accordance with small values of the corresponding entropy change ($\Delta S \leq 0.5R$), all of these transformations were considered as belonging to the displacive type [5,6].

Monoclinic phase in K_2TaF_7 remains stable when cooled to at least 100 K [7] and, upon heating, potassium heptaflurotantalate undergoes two structural phase transitions [8]. One of them takes place at 998 K which is very close to the point of the incongruent melting at 1022 K and accompanied by the mass loss. This is the reason why the main attention of investigators is usually paid to the reveres structural transformation $P2_1/c$ ($T_0 = 475$ K) – $Pnma$ (Z=4) [4] which is rather unusual in respect to the following intriguing points. (1) Space groups $P2_1/c$ and $Pnma$ are connected by the group–subgroup relation, however, the large structural distortions in monoclinic phase and huge thermal hysteresis were found [8] which are typical for reconstructive phase transition. (2) Despite the absence of structural disorder in phase $Pnma$ [9], large entropy change, $\Delta S = R \ln 6$, obtained using differential scanning calorimeter (DSC), is characteristic for order–disorder transformation [8]. This contradiction can be explained taking into account a giant change in the volume of the anionic polyhedron as well as the coordination number of the central atom Ta. (3) The origin of structural distortions was characterized as "proper" ferroelastic and a significant change in the phase transition parameter η was found in a wide range of temperatures below T_0. But the temperature dependent part of the corresponding entropy $\Delta S(T) \sim \eta^2(T)$ was detected in DSC measurements only in rather narrow temperature region [8]. (4) Heat treatment causes changes in the temperature and enthalpy of the phase transition, but does not change the corresponding entropy [7].

Due to a large change in entropy during the phase transition, it is possible to assume a very high barocaloric efficiency of K_2TaF_7. However, to analyze the intensive and extensive barocaloic effects (BCE), detailed information is needed on the temperature dependencies of entropy and elastic deformation, as well as on the sensitivity of the temperature of the phase transition to external pressure.

In the present paper, we carried out thorough studies of the heat capacity and thermal expansion in a wide temperature range which allowed one to determine the main thermodynamic parameters of the phase transition $P2_1/c$ – $Pnma$. We also evaluated the baric coefficient, dT_0/dp, characterizing stability of the crystal lattice in respect to hydrostatic pressure as well as intensive ΔT_{AD} and extensive ΔS_{BCE} BCE.

Sample preparation and measurement technique

Sample preparation and characterization

Potassium heptafluorotantalate was prepared by its precipitation from hydrofluoric acid solution. A starting material, Ta_2O_5, of a reagent grade was dissolved

in concentrated HF (40% wt) at heating followed by addition of KCl. A stoichiometric quantity of potassium salt was added to the solution diluted with water In accordance with the reaction: H_2TaF_7+2KCl=K_2TaF_7+2HCl. The crystalline precipitate was filtered of and washed under vacuum with alcohol. Using EDX and XPS methods, the composition of the crystals was checked. Both indicated the oxygen presence. The fluorine amount was determined by a fluoride ion-selective electrode calibrated with different diluted solutions of standard NaF. The real content of fluorine was 31.5±0.4% (compared to the calculated 33.92% for K_2TaF_7). Thus, the composition of the crystals grown is $K_2TaO_{0.3}F_{6.4}$.

X-ray studies were performed to make sure that such an amount of oxygen impurity does not affect the type of structure. All peaks on the powder diffraction patterns were indexed by monoclinic cell $P2_1/c$ with parameters close to previously found for K_2TaF_7 [2,10]. This crystal structure was taken as starting model for Rietveld refinement which was found to be stable revealing low R-factors (R_{wp}=5.81%, R_p=4.64%, χ^2=1.63). Thus, we can use the stoichiometric formula K_2TaF_7.

Dilatometry

Measuring the thermal expansion was performed using a push-rod dilatometer (NETZSCH model DIL-402C) with a fused silica sample holder. Experiments were carried out in the temperature range of 100–750 K with a heating rate of 3 K·min^{-1} in a dry He flux. The results were calibrated, by taking quartz as the standard reference in order to eliminate the influence of thermal expansion of the system. The reproducibility of data obtained in all successive series of measurements was not less than 5%. Samples for dilatometric measurements were prepared as quasi-ceramic disc-shaped pellets of 6 mm diameter and 1.3 mm thickness.

Calorimetry

Detailed measurements of heat capacity, $C_p(T)$, of K_2TaF_7 were performed in a wide temperature range of 4–600 K by means of three calorimetric methods.

Below 90 K, the dependence $C_p(T)$ was studied using a special option of a Physical Property Measurement System (PPMS, Quantum Design, USA). Measurements were performed on a ceramic sample. Apiezon N grease was used to provide reliable thermal contact between the sample and the additives. The relative error of measurements was less than 1%.

A homemade adiabatic calorimeter with three screens, as described in Ref. [11], was used in experiments between 80 and 320 K. The heat capacity of the "sample + heater + contact grease" system was measured using discrete as well as continuous heating. In the former case, the temperature step was varied from 1.5 to 3.0 K. In the latter case, the system was heated at rates of about 0.15–0.30 K·min^{-1}. The heat capacities of the heater and contact grease were determined in individual experiments. The inaccuracy in the heat capacity determination did not exceed 0.5–1.0%.

The high-temperature heat capacity was measured by DSC on a NETZSCH 204 F1 instrument in a dry helium flow (20 ml·min^{-1}) in the 300–600 K temperature

range at a heating rate of 5 K·min^{-1} with the accuracy ∼2%. Sapphire was used as the standard.

Results and discussion

Thermal dilatation

Results of two consecutive dilatometric experiments are presented in Fig. 1. In the first heating mode measurements were started from 100 K. Temperature behavior of the coefficient of volume thermal expansion, β, and volumetric strain, $\Delta V/V = 3(\Delta L/L)$, shows only one anomaly at $T_0 = 486 \pm 1$ K. According to very large value of the thermal hysteresis $\delta T_0 \approx 50$ K [8], the phase transition should take place upon cooling at 436 K. Due to the specific features of the dilatometric installation, measurements in the cooling mode can be carried out only down to ∼450 K and as a result no anomalies were detected upon cooling. During the second heating, started from 300 K, a more pronounced negative anomaly $\Delta\beta$ was observed, which is about two times larger than the anomaly during the first heating. The observed difference may be due to the residual mechanical stresses arising in the quasi–ceramic sample during its preparation and their annealing during the first heating to 750 K.

In accordance with the first order $Pnma - P2_1/c$ transformation, strong anomalous behavior in the volume strain was observed in the narrow temperature range around T_0 with the negative strain jump $\delta V_0/V = -(36 \pm 5) \times 10^{-3}$ (Fig. 1(b)). This value gives the dominant contribution to the total change in the volume strain and clearly indicates that the phase transition is far from the tricritical point where $\delta V_0/V \to 0$.

Heat capacity

Good agreement was found between the results of calorimetric measurements performed by three different methods. The behavior of the molar heat capacity in the entire temperature range studied is shown in Fig. 2(a) and demonstrates, firstly, the stability of the monoclinic phase $P2_1/c$ to very low temperature (4 K), and, secondly, the existence of only one strongly asymmetric heat capacity anomaly above room temperature corresponding to the $Pnma - P2_1/c$ phase transition. The temperature of the $C_p(T)$ maximum, $T_0 = 486.2 \pm 0.5$ K, agrees well with the value of the phase transition temperature found in dilatometric measurements and turned out to be slightly lower than T_0 observed in optical experiments on single crystals (503–508 K) [7]. To determine the hysteresis value δT_0 in the sample under study, we performed measurements using DSC. Fig. 3 shows the temperature dependence of DSC signal measured in heating and cooling modes. At thermal cycling rate equal to $dT/dt = 5$ K·min^{-1}, the DSC peaks corresponded to phase transition temperature were found at 484.5±1 K and 447.5±1 K upon heating and cooling, respectively. The observed value $\delta T_0 \approx 37$ K shows why a structural transformation was not detected in dilatometric experiments during the cooling process.

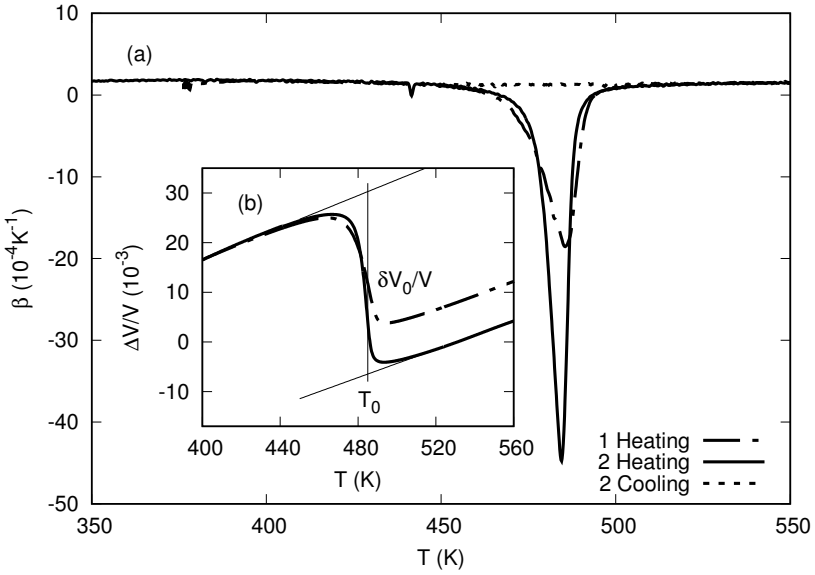

Fig. 1 Temperature dependencies of thermal expansion coefficients β (a) and the volume strains $\Delta V/V$ (b) of K_2TaF_7. Dashed line is lattice contribution $\beta_L(T)$ that coincides with the behavior of $\beta(T)$ measured in cooling mode

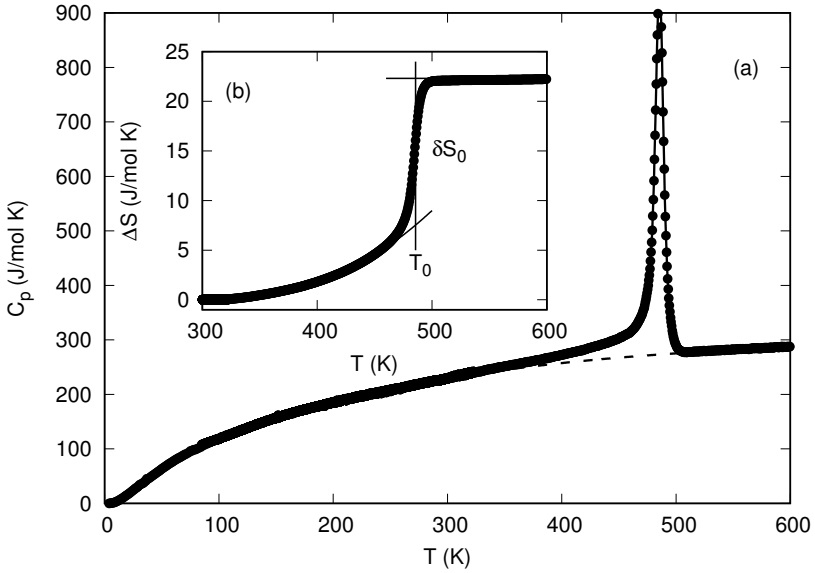

Fig. 2 Temperature dependencies of the molar heat capacity (a) and anomalous entropy (b) of K_2TaF_7. Dashed line corresponds to the lattice heat capacity C_L

To get information about the entropy of the phase transition, it was necessary to separate the anomalous, ΔC_p, and lattice, C_L, contributions to the total heat capacity, C_p, of K_2TaF_7.

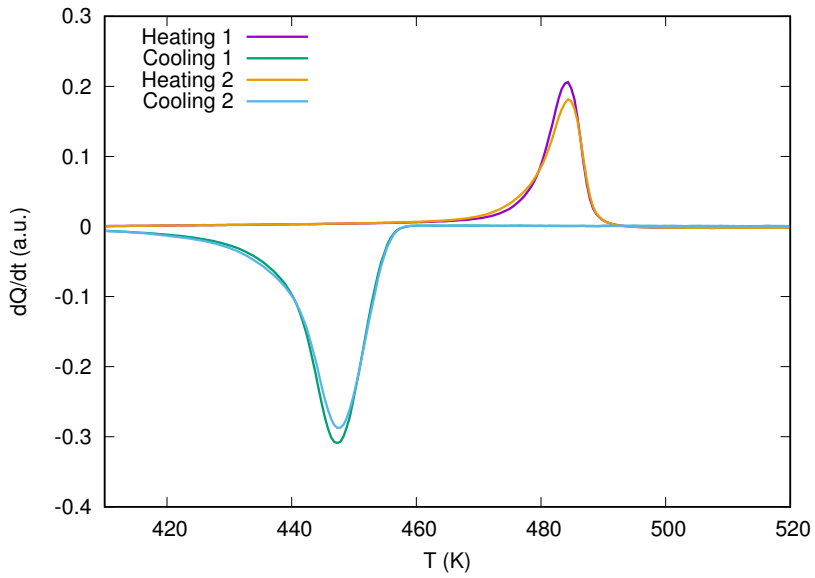

Fig. 3 Temperature dependencies of dQ/dt measured in DSC experiments upon heating and cooling at the rate 5 K·min^{-1}

This procedure was carried out using a simple model describing $C_L(T)$. The experimental data taken far from the transition points ($T < 300$ K and $T > 510$ K) were fitted using a linear combination of Debye and Einstein terms $C_L = K_D C_D + K_E C_E$, where

$$C_D(T) = 9R\left(\frac{T}{\Theta_D}\right)^3 \int_0^{\Theta_D/T} \frac{x^4 \exp(x)}{(\exp(x)-1)^2} dx, \quad (1)$$

$$C_E(T) = 3R\left(\frac{\Theta_E}{T}\right)^2 \frac{\exp(\Theta_E/T)}{(\exp(\Theta_E/T)-1)^2} \quad (2)$$

and K_D, K_E, Θ_D, Θ_E are fitting parameters.

The average deviation of the experimental data from the smoothed curve does not exceed 1%. The lattice contribution is shown by a dashed line in Fig. 2(a). The anomalous heat capacity, $\Delta C_p = C_p - C_L$, was observed in very wide temperature range below the phase transition point $T_0 - 140$ K which correlates with the behavior of the phase transition parameter [7].

Fig. 2(b) demonstrates the temperature behavior of excess entropy associated with the phase transitions in K_2TaF_7, determined by integration of the area under the ΔC_p versus T curve: $\Delta S_0 = 22.3 \pm 2.0$ J·(mol·K)$^{-1}$. The entropy jump associated with the first order phase transition was estimated to be equal approximately $\delta S_0 = 14.5 \pm 2.0$ J·(mol·K)$^{-1}$ (Fig. 2(b)).

Significant changes in entropy ($\Delta S_0 \approx R \ln 16$) and cell volume ($\delta V_0/V \approx 3.6$ %) during phase transformation indicate that the distortions of the structure can be associated with the order–disorder processes. However, analysis of structural data [9] showed that in the high-temperature phase there is no disordering

of any structural elements, the ordering of which could lead to an order–disorder transition. At the same time, in the $P2_1/c$ phase, the displacements of all atoms turned out to be anomalously large.

It can be assumed that the cause of anomalously large entropy can be, firstly, a pronounced (but not extreme, leading to disordering) anharmonicity of atomic vibrations in the *Pnma* phase, and secondly, the reconstructive nature of the transition accompanied by a giant jump in volume. It should be noted, however, that this is an unusual reconstructive transition, since the symmetries of the high-temperature and low-temperature phases are related by the group–subgroup relation.

Thus, the mechanism of the phase transition in K_2TaF_7 is very complex and remains uncertain to date.

Effect of hydrostatic pressure

Calorimetric and dilatometric studies have provided reliable evidence of the first order of phase transition in K_2TaF_7. The susceptibility of transformations of this kind to hydrostatic pressure can be determined within the framework of the Clausius–Clapeyron equation, using the heat capacity and thermal dilatation data

$$\frac{dT_0}{dp} = \frac{\delta V_0}{\delta S_0} = V_m \frac{\delta V_0/V}{\delta S_0}, \tag{3}$$

where V_m – molar volume and δS_0, δV_0 are entropy and volume jumps at T_0, respectively. Estimation of the derivative of the transition temperature with respect to pressure gives the value $dT_0/dp \approx -220 \pm 20$ K·GPa^{-1}.

To more correctly determine the magnitude of the baric coefficient, one can use the Pippard relation, which relates the temperature dependencies of the thermal expansion coefficient and heat capacity in the vicinity of the phase transition

$$C_p = \frac{V_m T_0}{\gamma}\beta + const, \quad \gamma = \frac{dT_0}{dp}. \tag{4}$$

Because the value of dT_0/dp is strongly depend on the data close to the phase transition point, small errors in temperature scales of measurements of heat capacity (temperature sensor – platinum thermometer) and thermal expansion (temperature sensor – thermocouple) will lead to significant errors in the results obtained using the Pippard relation. In this regard, the data on the thermal expansion and heat capacity were reduced to one temperature scale by alignment of the phase transition temperatures.

The results of joint analysis of dependencies of $C_p(T)$ and $\beta(T)$ below T_0 are shown in Fig. 4. The experimental points fall on a straight line which means that the Pippard relation is fairly satisfied in rather wide temperature range $T_0 - T$=(5–35) K. Deviations from linear behavior are observed near T_0, where the imperfections of the sample, the dynamic mode of the thermal expansion measurements, and the difference in temperature scales for $C_p(T)$ and $\beta(T)$ measurements play a significant role. The obtained value of the baric coefficient $dT_0/dp \approx -212 \pm 15$ K·GPa^{-1} agrees well with that calculated from the Clausius–Clapeyron equation and gives us hope that the value of dT_0/dp is close to real one as well.

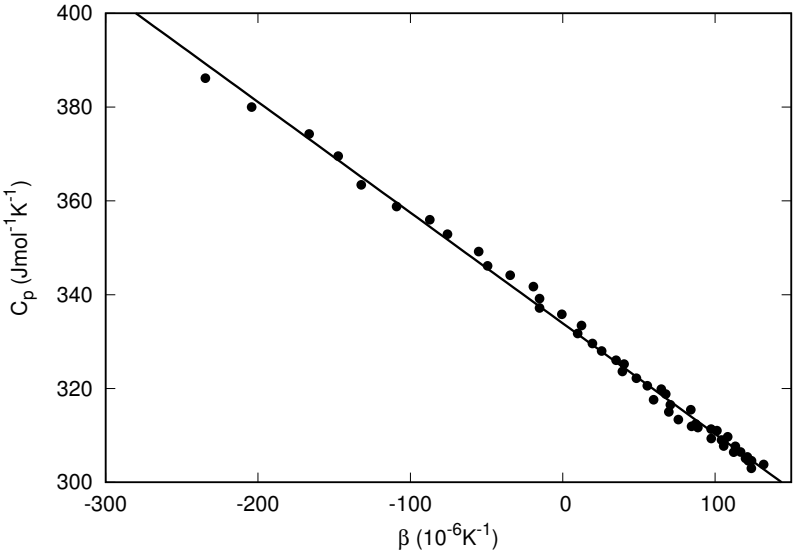

Fig. 4 The relationship between the molar heat capacity and the coefficient of volume thermal expansion below T_0

A negative sign and a large value of dT_0/dp indicate the possibility of a shift of the $Pnma - P2_1/c$ phase transition to room temperature under pressure of about 1 GPa. Due to the combination of large values of ΔS_0 and dT_0/dp, the barocaloric efficiency of K_2TaF_7 turns out to be very high.

Barocaloric effect

Barocaloric effect is associated with the reversible change in entropy, ΔS_{BCE}, or temperature, ΔT_{AD}, of a thermodynamic system with a change in pressure under isothermal or adiabatic conditions, respectively. An important characteristic of barocaloric efficiency is also a minimum pressure, p_{min}, required to implement maximum values of the extensive, ΔS_{BCE}^{max}, equal to the phase transition entropy, and intensive, ΔT_{AD}^{max}, effects. In the case of the strictly first order phase transition, the relations between these three parameters are as follows [12,13]:

$$p_{min} \geq \frac{T\Delta S_0}{C_L dT_0/dp}, \quad \Delta T_{AD}^{max} \approx \frac{dT_0}{dp} p_{min} \tag{5}$$

Using the values C_L, ΔS_0 and dT_0/dp determined above for K_2TaF_7, we have found: $p_{min} \approx 0.2$ GPa and $\Delta T_{AD}^{max} \approx -35 \pm 2$ K. The negative sign of the intensive BCE is associated with a decrease in the volume at the phase transition.

The behavior of both intensive and extensive BCE with change in pressure and temperature was analyzed in the framework of the previously described method [14]. For this aim, temperature dependencies of the total entropy under different pressure (Fig. 5(a)) were determined by summation of the lattice entropy S_L =

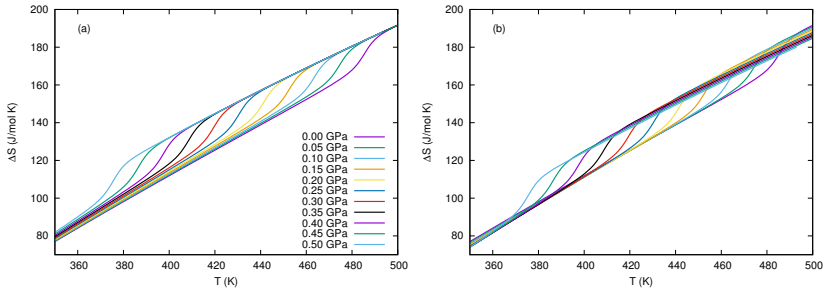

Fig. 5 Temperature dependencies of total entropy of K_2TaF_7 at different hydrostatic pressure before (a) and after (b) correction for the additional lattice entropy changes with pressure

$\int(C_L/T)dT$ and the anomalous contribution $\Delta S(T)$ determined at $p = 0$ and shifted along the temperature scale according to the sign and value of dT_0/dp.

Recently, studies of differential thermal analysis under pressure for some complex fluorides and oxyfluorides revealed the absence of the pressure effect, at least to 0.6 GPa, on the phase transition entropy [14–16]. Taking into account these results, we assumed that in the case of K_2TaF_7 pressure also does not affect ΔS.

The behavior of the extensive BCE determined using temperature and pressure dependencies of the total entropy $\Delta S_{BCE} = S(T,p) - S(T,p=0)$ is shown in Fig. 6(a). To obtain correct information on $\Delta T_{AD}(T,p)$, plots of $S(T,p) = S_L(T,p) + \Delta S(T,p)$ were analyzed based on the condition of constant entropy $S(T,p) = S(T + \Delta T_{AD}, p = 0)$ (Fig. 6(b)).

At the first stage, we did not take into account the changes in the lattice entropy with pressure (Fig. 5(a)). The magnitudes of ΔS_{BCE} and ΔT_{AD} increase with increasing pressure tending to maximum values but not reaching them at 0.5 GPa which is higher than p_{min} (Fig. 6(a),(b)). The difference between estimated p_{min} and experimental pressure is particularly associated with the validity of Eq. 5 for strong first order phase transition whereas K_2TaF_7 undergoes transformation close enough to the tricritical point. Nevertheless, the analysis showed the possibility of realizing very large values of both BCE, $\Delta S_{BCE} \approx 21$ J·(mol·K)$^{-1}$=54 J·(kg·K)$^{-1}$ and $\Delta T_{AD} \approx -30$ K, in this crystal at rather low pressure $p \sim 0.5$ GPa. The intensive BCE is in good agreement with the maximum possible value ΔT_{AD}^{max} estimated above. It is necessary to point out, that intensive and extensive BCE found in K_2TaF_7 are comparable and in some cases even exceed barocaloric parameters in other materials [17–20].

On the other hand, the crystal lattice of potassium heptafluorotantalate is characterized by positive volume deformation $\Delta V_L/V > 0$ and large volumetric thermal expansion coefficient $\beta_L \approx 1.5 \times 10^{-4}$ K^{-1}. In accordance with the Maxwell equation:

$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p \qquad (6)$$

this peculiarity leads to significant conventional contribution ($\Delta S_{BCE} < 0$, $\Delta T_{AD} > 0$) associated with the crystal lattice expansion to the total BCE and as result decreases the extensive and intensive inverse BCE in the phase transition region.

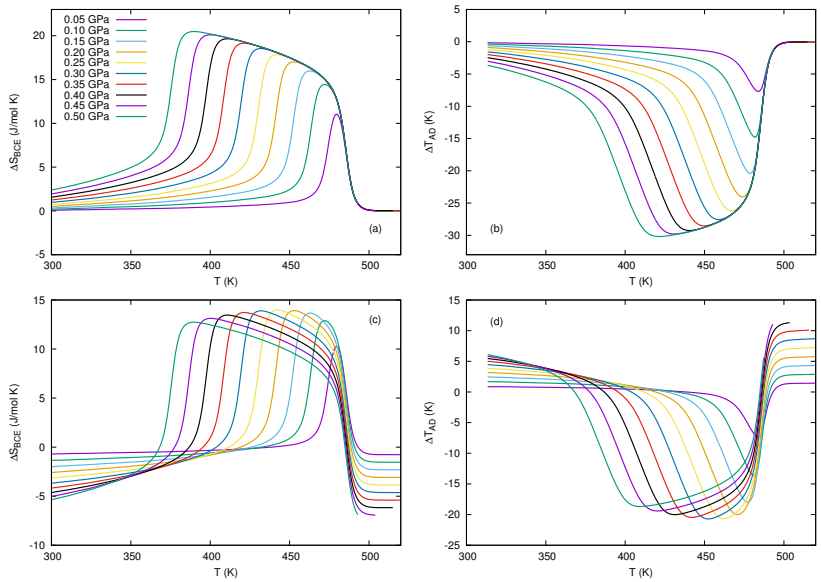

Fig. 6 Temperature dependencies of barocaloric entropy and temperature changes at different hydrostatic pressure before (a, b) and after (c, d) correction for the additional lattice entropy changes with pressure

Thus, to get detailed and correct information about BCE, it is necessary to know the pressure dependence of the total entropy. Due to a lack of opportunity to measure $C_p(T,p)$, the lattice entropy change with pressure, ΔS_L, may be expressed using Eq. 6 with S replacing by S_L

$$\Delta S_L(T,p) = -\int_0^p (\partial V_L/\partial T)_p dp \approx -V_m \beta_L(T) p, \tag{7}$$

We assume here that pressure not significantly affect β_L and V_m.

Fig. 5(b) shows the temperature dependencies of the total entropy at different pressures taking into account changes in the lattice entropy under pressure. The temperature and pressure dependencies of both the extensive and the intensive BCE determined in this approximation, are shown in Fig. 6 (c) and (d). It can be seen that in this case the behavior of $\Delta S_{BCE}(T,p)$ and $\Delta T_{AD}(T,p)$ changed significantly and peak values ΔS_{BCE}^{max} and ΔT_{AD}^{max} decreased. However, a rather large conventional BCE appeared above the transition temperature. As a result, at $p = 0.5$ GPa, there are very rapid changes in the values of ΔS_{BCE} (from -7 to +14 J·(mol·K)$^{-1}$ or from -18 to +36 J·(kg·K)$^{-1}$) and ΔT_{AD} (from +12 to -20 K). Recently, similar effect of the lattice thermal expansion on BCE was observed in ferroelectric $(NH_4)_2SO_4$ [17].

The phenomenon of a change in the sign of BCE in a narrow temperature range was observed by us earlier in the vicinity of the triple points on the $T-p$ phase diagrams for a series of fluorides and oxyfluorides [12,13]. The results obtained in the present paper and [12] are very important and promising from the point of view of searching new materials with large BCE and designing original cooling

cycles. It is obvious that in materials characterized by an increase in the volume of the unit cell during the phase transition and a large value of the positive coefficient of volume thermal expansion far from the transition point, BCE will increase due to the high compliance of the lattice entropy to the pressure.

Conclusions

Studies of thermal expansion and heat capacity of potassium heptafluorotantalate, K_2TaF_7, performed in a wide temperature range allowed us to establish the following important points.

Calorimetric measurements showed the stability of the phase $P2_1/c$ to very low temperature (∼4 K). The phase transition $P2_1/c - Pnma$ (Z=4) is a pronounced first order transformation accompanied by large values of thermal hysteresis ($\delta T_0 \approx$37 K) and entropy ($\Delta S_0 = 22.3 \pm 2.0$ J·(mol·K)$^{-1}$) as well as jumps of volume ($\delta V_0/V = -(3.6 \pm 0.5)\%$) and entropy ($\delta S_0 = 14.5 \pm 2.0$ J·(mol·K)$^{-1}$) at T_0=486.2 K. Anomalous behavior of the heat capacity and entropy is observed in very wide temperature range below the phase transition point $T_0 - 140$ K which correlates with the behavior of the parameter of the phase transition [7].

A very high sensitivity of the transition temperature to hydrostatic pressure was found. Good agreement is observed between the values dT_0/dp determined using the Pippard (-212±15 K·GPa^{-1}) and Clausius–Clapeyron (-220±20 K·GPa^{-1}) equations. A large value and a negative sign of the baric coefficient indicate the possibility of a shift of the $Pnma - P2_1/c$ transformation to room temperature under pressure of about 1 GPa.

Due to the combination of large values of ΔS_0 and dT_0/dp, K_2TaF_7 demonstrates very high barocaloric efficiency. It was shown that large thermal expansion of the crystal lattice leads to large contribution of the conventional BCE to the total effect. The conversion from the conventional BCE to the inverse is observed in narrow temperature range and accompanied by large change of intensive and extensive effects. These results show that barocaloric efficiency can be increased in materials with conventional BCE and large positive value of β_L.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflicts of interest.

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