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Heat capacity and p – T phase diagrams of the ordered perovskites Pb_2MgWO_6 and Pb_2CoWO_6

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Abstract. The heat capacities of Pb_2MgWO_6 and Pb_2CoWO_6 and the effect of hydrostatic pressure on the phase transitions have been studied on powdered samples by means of an adiabatic calorimeter and DTA performed under pressure, respectively. Thermodynamic parameters, such as change of total excess entropy, latent heat and hysteresis of the phase transition temperature were determined. Entropies and p – T phase diagrams are discussed in connection with structural data.

1. Introduction

Many oxides of the type $\text{A}_2\text{B}'\text{B}''\text{O}_6$ crystallize in the perovskite-like structure and can undergo phase transitions (PTs) of various kinds. Cation ordering may occur, depending on the ionic radii and the charges of B-site cations, giving rise to different structural characteristics. The degree of long-range order between the species B' and B'' affects the behaviour of the physical properties as a function of temperature. Partially or fully disordered compounds exhibit diffuse PTs and relaxor phenomena. Ordered compounds undergo sharper transitions, the sequence of which is also strongly dependent on the cations involved. In the series of lead-based elpasolites, Pb_2MgWO_6 (PMW) and Pb_2CoWO_6 (PCW) present a very high degree of B-site ordering and they have the cubic structure $Fm\bar{3}m$ ($Z = 4$) at high temperatures [1–5].

For many years, PMW was believed to exhibit a cubic–orthorhombic PT of the first order at about 311 K (T_1). The orthorhombic phase is antiferroelectric [3, 6–8]. Based on the results of electron diffraction studies, the existence of an intermediate phase was proposed in a narrow temperature range just below T_1 [2]. Structure refinement performed by both x-ray and neutron diffraction studies showed no difference between the powder patterns at 80 and 294 K [1]. The extinction conditions indicated that the space groups are $Pm\bar{c}n$ ($Pnma$) or $P2_1cn$ ($Pna2_1$). The centrosymmetric space group $Pm\bar{c}n$ was chosen, in agreement with the antiferroelectricity of this phase. A soft mode was observed in Raman scattering measurements on powdered samples, which suggested that the transition at T_1 has a displacive behaviour [9]. Further investigations on single crystals have shown some peculiarities in the Raman spectra and dielectric properties at about 240 K, which were presumed to be associated with the existence of an intermediate phase between the cubic paraelectric and antiferroelectric phases [10].

In the first studies on PCW, by x-ray and dielectric measurements, a phase transition at about 300 K (T_1) was found [11–13]. An orthorhombic symmetry was proposed for the phase below T_1 . This phase was found to be antiferroelectric and assumed to transform into a ferroelectric phase below 77 K [11, 13]. Dielectric permittivity and thermal dilatation studies

have revealed, in addition to the anomaly due to the PT at T_1 , another anomaly at about 253 K (T_2). The latter anomaly was explained as being associated with the transformation between the two antiferroelectric phases [14]. A new insight on the symmetry of PCW below T_1 is provided by the results of x-ray, neutrons, optical studies and electron microscopy [15–17]. Superstructure reflections and domain patterns observed below T_1 have indicated that the phase (2) between T_1 and T_2 is incommensurate with a monoclinic average symmetry [15, 17]. Below T_2 the symmetry is orthorhombic [16, 17]. The domain and neutron diffraction patterns were unchanged between 250 and 4 K indicating that there are no additional structural PTs in that range. Anomalies connected with the succession of two PTs were also observed in birefringence and differential scanning calorimetry (DSC) measurements [16]. Rather unusual behaviour of the remnant spontaneous polarization was observed between 4 and 240 K [16]. Nevertheless, the orthorhombic phase (3) was presumed to be ferroelectric. According to [18], the space group of this phase could be either $Pm\bar{c}n$ or $P2_1cn$ in connection with antiferro- and ferroelectricity, as assumed in [14] and [16], respectively. It is worth noting that rather different values of PT temperatures T_1 and T_2 have been reported for PCW in the literature. However, as was discussed in [19], this was attributed to synthesis problems. Single crystals obtained by the flux method presented the same transition temperature T_1 but a large dispersion of the transition temperature T_2 and a wide variation in the temperature range of the coexistence of phases 2 (incommensurate phase) and 3 (orthorhombic phase) was observed.

The cubic–orthorhombic PT in PMW is not so sample-dependent since most studies give T_1 in a range between 310 and 312 K. The principal point of discussion concerning this compound is the existence of the intermediate phase.

As far as we know, there are no detailed data for PMW and PCW concerning thermodynamic properties. These properties can be considered as universal ones, exhibiting an anomalous behaviour irrespective of the nature of the PT. Information about heat capacity was only obtained by DSC on PCW [16] and by an adiabatic calorimeter on PMW [20]. The latter measurements were performed in a rather narrow temperature range (275–311 K) on a ceramic sample, which was believed by the authors [20] to be inhomogeneous. The pressure effect on PT temperature has been studied by measurements of dielectric properties on ceramic samples of both elpasolites [8, 21, 22], but there is some disagreement between the experimental data for PMW obtained in [8, 21].

In this paper we report the results of thermodynamic studies over a wide temperature range on powdered samples of PMW and PCW.

2. Experimental

For PMW we have used the same powder as in the structural [1] and Raman studies [9]. This powder was synthesized by the usual techniques, starting from stoichiometric quantities of reagents PbO, WO₃ and MgO of the highest purity. It is more difficult to obtain PCW powder free of the pyrochlore phase by the same technique. Therefore, a powder sample was prepared by grinding single crystals which were grown by the flux method [23] and which have previously been used in structural studies [5, 17–19]. No impurities were detected and no evidence of Mg/W or Co/W disorder was found. So both PMW and PCW samples are highly ordered perovskites in the temperature range of thermodynamic studies performed in the present paper. Previous x-ray analyses [19] have shown that the single crystals PCW used in this study are characterized by weak dispersion of PT temperatures T_1 and T_2 so they are homogeneous and free of mechanical stresses.

The heat capacity was measured with an adiabatic calorimeter in the temperature range 100–370 K. Powdered samples of mass 4.297 g (PMW) and 0.860 g (PCW) were set into an

indium container sealed under helium atmosphere. Continuous and/or stepwise temperature changes were used.

The effect of hydrostatic pressure was also studied on powdered samples which have been used for calorimetric measurements. The variation of PT temperatures was measured by means of differential thermal analysis (DTA). Pressure up to 0.6 GPa was generated inside the piston- and-cylinder type vessel associated with the multiplier. Silicon oil was used as the pressure-transmitting fluid. Owing to the high sensitivity, a germanium–copper thermocouple was utilized as a differential device. Quartz used as a reference substance and a small copper container ($\sim 0.05 \text{ cm}^3$) filled with the powdered sample were fixed with glue onto two thermocouple junctions. Pressure and temperature were measured with a manganin gauge and copper–constantan thermocouple, respectively, with inaccuracies of about $\pm 10^{-3}$ GPa and ± 0.3 K.

3. Experimental results

3.1. Heat capacity

The heat capacities of both ordered perovskites measured on heating are shown in figures 1 and 2.

In PMW no anomaly other than heat capacity peak associated with PT from the cubic phase was found (figure 1). The average deviation of the experimental data from the smoothed curve was about 0.5% and not more than 0.25% in continuous and stepwise measurements, respectively. The PT temperature found in the present measurements, $T_1 = 312.8 \pm 0.2$ K, agrees well with the value for T_1 reported in [6]. Using continuous heating and cooling (the inset of figure 1) with a small rate of about $\pm 2.5 \times 10^{-2} \text{ K min}^{-1}$, the latent heat $\delta H_1 = 2340 \pm 200 \text{ J mol}^{-1}$ and the thermal hysteresis $\delta T_1 = 2.45 \pm 0.2$ K were measured.

In PCW two heat capacity anomalies were observed at $T_1 = 302.7 \pm 0.5$ K and $T_2 = 256.2 \pm 0.5$ K (figure 2). The hysteresis of the PT temperature $\delta T_1 \approx 1$ K was measured in the same way as for PMW. Since the value δT_2 can be about 10 K [19], a stepwise cooling process was used to measure such a large hysteresis. The results of the measurements near T_2 are presented in the inset in figure 2, with a value of δT_2 of 11.4 K. Because of the rather small mass of the PCW sample and hence the small heat capacity in comparison with that of the indium container, it was impossible to determine the values of the latent heat for both PTs by continuous heating.

A fit of experimental data taken far from the PT points using Debye's and Einstein's functions, $C_{lat}(T) = A_1 D(\theta_D/T) + A_2 E(\theta_E/T)$, allowed us to separate the lattice, C_{lat} , and anomalous, ΔC_p , contributions. The dashed lines in figures 1 and 2 show C_{lat} . As observed in figures 3(a) and (b), an excess heat capacity for both PMW and PCW exists almost in the same wide temperature range. In the case of PMW (figure 3(a)), one can see that there is no peculiarity in the excess heat capacity behaviour, neither around 240 K nor near the PT point where some transformations are supposed to take place according to [2, 10].

Integration of the area under the $\Delta C_p/T$ versus T curve was performed in order to determine the entropy change. For PMW this value was calculated to be $\Delta S_1 = 14.1 \pm 1.2 \text{ J mol}^{-1} \text{ K}^{-1}$. For PCW we could determine, in the same way, only the sum of the total entropy changes $\Sigma \Delta S_i = 11.1 \pm 1.7 \text{ J mol}^{-1} \text{ K}^{-1}$ associated with a succession of PTs. However, one can see that the heat capacity peak at T_2 seems to appear on the 'tail' of the excess heat capacity associated with the PT at T_1 . This peak is narrow, symmetric and owing to the large δT_2 hysteresis, it could be considered as connected with a strong first order transformation far from the tricritical point. In this case the total entropy change is equal to a 'jump' value at T_2 : $\Delta S_2 = \delta S_2 = 1.5 \pm 0.2 \text{ J mol}^{-1} \text{ K}^{-1}$. So the value ΔS_1 is about $9.6 \text{ J mol}^{-1} \text{ K}^{-1}$.

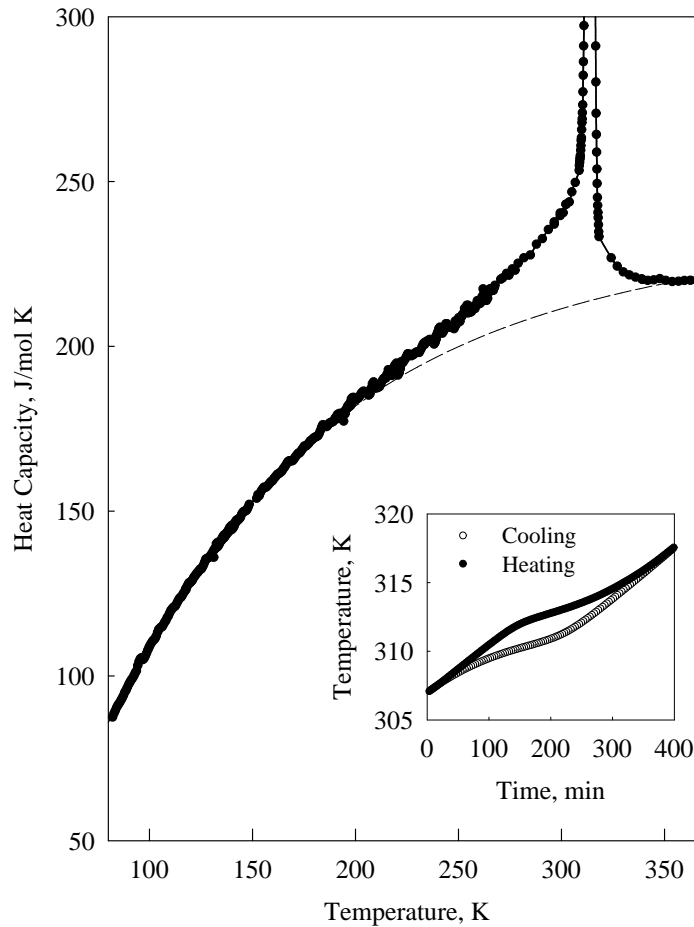


Figure 1. The heat capacity of PMW. The broken curve is the lattice heat capacity. The inset shows the results of continuous heating and cooling around T_1 .

3.2. Pressure effect

The p - T phase diagrams of PMW and PCW obtained from DTA measurements are shown in figure 4. On the whole, these results are in rather good agreement with those obtained by dielectric measurements [8, 21]. No DTA anomalies, which might be related to pressure-induced PTs are observed up to about 0.6 and 0.47 GPa, for PMW and PCW, respectively. We did not find a tendency to saturation of the dT_1/dp value of PMW at pressures above 0.2 GPa, as was reported in [22]. In addition, unlike data reported in [8, 21], all PT temperatures of both PMW and PCW show nonlinear behaviour in the whole pressure range.

In PMW, the pressure dependence of the PT temperature between phase 1 and phase 2 is approximately described by the expression

$$T_1 = a + bp + cp^2 \quad (1)$$

where $a = 312.5 \pm 0.2$ K, $b = -32.8 \pm 1.5$ K GPa $^{-1}$, $c = -12.1 \pm 2.2$ K GPa $^{-2}$. The measured value b of the initial slope of the phase boundary is close to the $dT_1/dp = -38 \pm 2$ K GPa $^{-1}$ value previously reported in dielectric measurements [8].

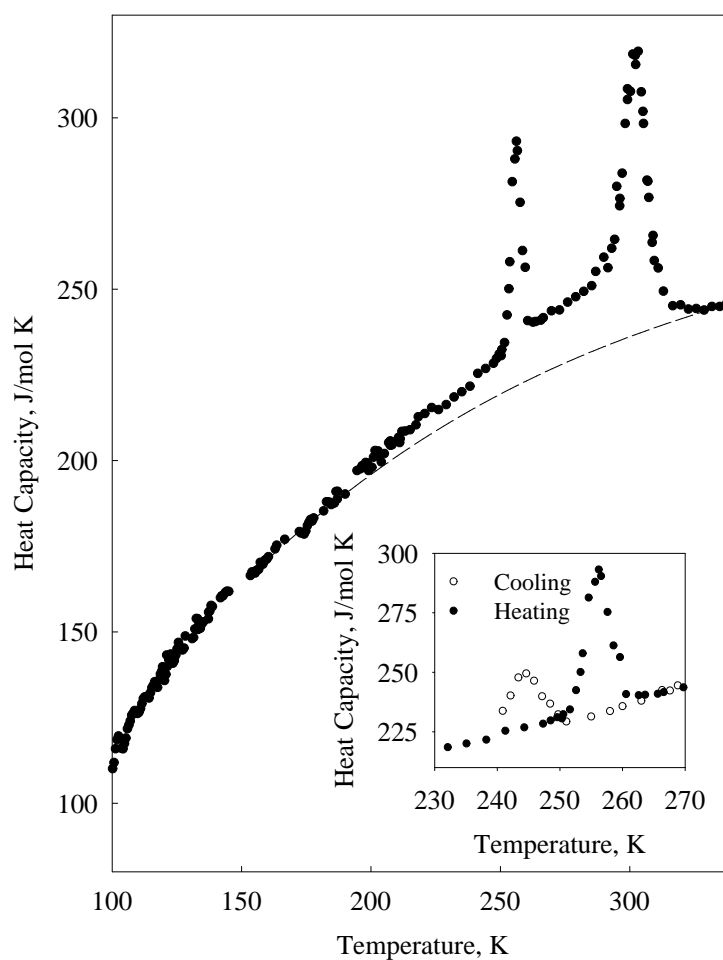


Figure 2. The heat capacity of PCW. The broken curve is the lattice heat capacity. The inset shows the results of stepwise heating and cooling around T_2 .

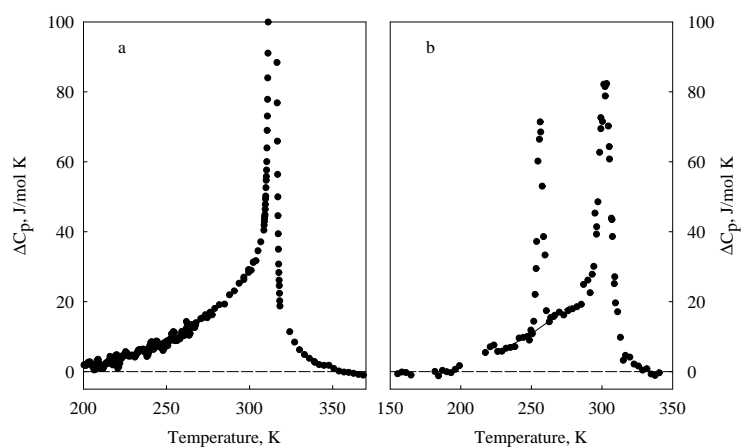


Figure 3. Excess heat capacity of PMW (a) and PCW (b).

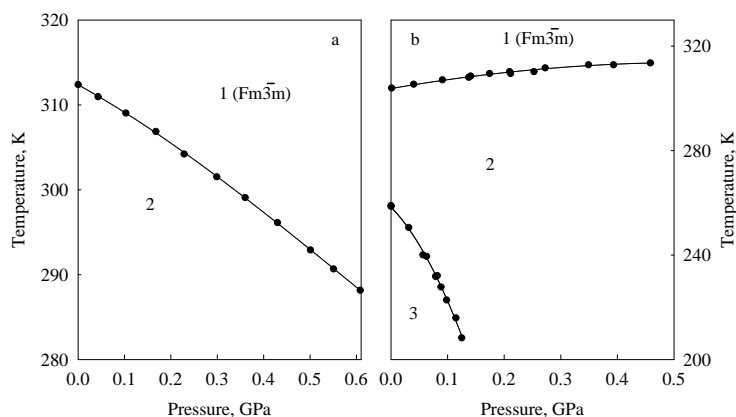


Figure 4. p - T phase diagrams of PMW (a) and PCW (b).

In PCW the transition temperature from phase 1 to phase 2 slightly increases with an increase in pressure (figure 4(b)). The value of dT_1/dp changes from 37.4 K GPa^{-1} at a pressure equal to zero up to about 5.3 K GPa^{-1} at 0.47 GPa . The range of stability of the incommensurate phase 2 expands with pressure. The negative slope of the boundary from phase 2 to phase 3 becomes steeper as the pressure increases. The pressure dependence of PT temperatures T_1 and T_2 can be described by (1) with the following values of the coefficients $a_1 = 303.8 \pm 0.6 \text{ K}$, $b_1 = 37.4 \pm 5.0 \text{ K GPa}^{-1}$, $c_1 = -35 \pm 10 \text{ K GPa}^{-2}$ and $a_2 = 258.3 \pm 1.0 \text{ K}$, $b_2 = -220 \pm 38 \text{ K GPa}^{-1}$, $c_2 = -1392 \pm 311 \text{ K GPa}^{-2}$, respectively. The measured value $b_1 = dT_1/dp$ agrees well with the value 30 K GPa^{-1} reported in [21]. The important difference between the values $(dT_2/dp)_{p=0}$ obtained in the present paper compared to those obtained in [21] (-148 K GPa^{-1}) can be explained by the strong dependence of PT at T_2 on the method of sample preparation.

4. Discussion

In PMW, no heat capacity anomalies associated with additional PTs were found either in calorimetric or in DTA measurements performed under pressure which means that if, as suggested in [2, 10], a second PT does exist, its excess entropy would be less than $10^{-2} \text{ J mol}^{-1} \text{ K}^{-1}$.

Up to now the nature of the PT at T_2 in PCW and the space group of the low temperature phase have not been determined exactly. If the latter was the same as in PMW, namely $Pm\bar{c}n$ [18], one could compare thermodynamic properties of both elpasolites. Considering the p - T phase diagrams and the total entropy changes of PMW and PCW one would expect a triple point associated with the appearance of an intermediate phase on the PMW diagram to be observed at the pressure increase (or volume decrease). In PCW such a triple point might exist in the negative pressure region (that is, the analogue of the unit cell volume increase). In this case, the phase diagram of PCW could be regarded as an extension of that of PMW in the high pressure region. However, it should be pointed out that the cubic unit cell parameter of PCW (0.8013 nm) [5] is a little larger than that of PMW (0.8006 nm) [1]. This fact is still not clearly understood and is not unique to this system since the same discrepancy was also observed in the series of $\text{CH}_3\text{NH}_3\text{PbX}_3$ perovskites [25].

The values of the latent heat δH_1 and the hysteresis of the PT temperature δT_1 obtained in PMW are nearly twice as large as those reported for ceramic samples [20]. From our point of

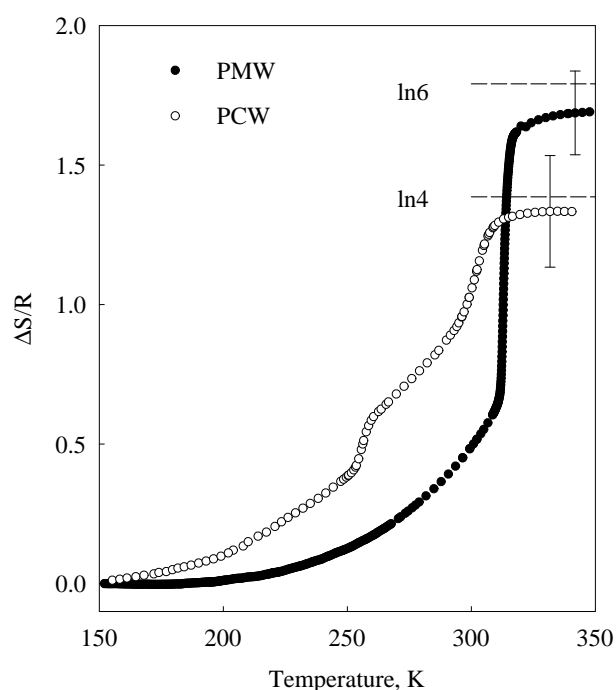


Figure 5. Temperature dependence of transition entropy of PMW and PCW.

view, this demonstrates that the quality of the powdered sample studied in the present work is higher than that of the ceramic. A decrease in the δT and δH values from sample to sample of the same composition could be related to smearing of PT caused by stresses and/or other imperfections.

The same effect was observed for entropy changes for both PTs in PCW measured in the present study relative to the DSC data [16]: $\Delta S_1 = 2.8 \text{ J mol}^{-1} \text{ K}^{-1}$ and $\Delta S_2 = 1.15 \text{ J mol}^{-1} \text{ K}^{-1}$. The latter are smaller because the DSC method allows one to detect the entropy change connected mainly with latent heat.

Using the Clausius–Clapeyron relation $dT/dp = \delta V/(V \times \delta S)$, one can evaluate a change in the unit cell volume at PT temperature. For PMW the calculated value $\delta V/V$ is about -0.32% and is in rather good agreement with $\delta V/V = -(0.26\text{--}0.47)\%$ obtained by x-ray measurements [8, 18]. In PCW the volume change calculated for the PT at T_2 $\delta V_2/V_2 = -0.43\%$ is almost half of the value -0.97% obtained in the x-ray study [19]. As already noted, δS_1 cannot be measured, but with dT_1/dp measured in the present study and $\delta V_1/V_1$ obtained in [19] it could be evaluated as $\delta S_1 = 2.9 \text{ J mol}^{-1} \text{ K}^{-1}$.

The temperature behaviour of the anomalous entropy of PMW and PCW is shown in figure 5. It is seen that the total values $\Sigma \Delta S/R$ of PCW and $\Delta S/R$ of PMW agree with each other, to within the experimental error. They are close to $\ln 4$ and/or $\ln 6$. Thus, according to the calorimetric data ($\Delta S/R \geq 1.39$), the PTs from the cubic phase in both elpasolites are order–disorder transitions. The small entropy change $\Delta S_2/R < 0.2$ at T_2 in PCW is characteristic of a PT of displacive type.

The mechanism of PTs in PMW and PCW could also be analysed using the results of x-ray, neutron and Raman studies [1, 5, 9, 10, 18, 19]. To reduce the reliability factor R and the thermal factors, which were abnormally high for Pb and O atoms, the crystal structures

of both ordered perovskites in the cubic phase have been described in terms of a disordered model [1, 5]. It was shown that the best results could be obtained when Pb and O atoms were assumed to be in a multi-minimum potential around their special positions. Oxygen atoms seemed to be distributed on rings lying in the planes orthogonal to the Mg(Co)–O–W direction. Three types of displacements, along the [100], [110] and [111] directions, leading to 6, 12 and 4 local disorder positions, respectively, were analysed for the Pb atoms. In PCW, the [110]_{Pb} model has shown the deepest minimum in *R*-factor versus Pb atom position [5]. A very weak difference between *R*-factors for three types of Pb displacements was found for PMW [1]. The authors have chosen the displacement along the [110] direction since this is associated with the largest Pb shift and the smallest thermal motion. As for the B-site cations, they were found to be ordered and placed in their special positions in the centre of the octahedra [1, 5].

At the same time, a soft mode corresponding to an oxygen octahedron rotation was found by inelastic neutron scattering in the cubic phase of PCW [24] and by Raman studies of orthorhombic phase in PMW [9, 10]. In PMW, weakly distorted MgO₆ and WO₆ octahedra tilt around the [100]_o direction by nearly 8.5° at 80 K [18]. Thus the mechanism of PT in PMW and PCW can be considered to be associated with both an order–disorder phase transition and a displacive phenomenon.

It is impossible to separate the experimental entropy change into two parts associated with each specific mechanism of PT. However, it is known that displacive PTs, connected with small octahedral tilts around one of the main axes of a cubic cell of perovskite-like crystals, are, as a rule, characterized by a rather small entropy change $\Delta S/R \leq 0.2$ [26]. The ordering process of Pb atoms therefore makes the main contribution to the PT entropy in PMW and PCW.

On the other hand, the experimental data concerning PT entropy in both elpasolites $\Delta S/R = \ln 4 - \ln 6$ show that, in the model considered, the Pb atoms are not completely ordered in the orthorhombic phase because otherwise the entropy value would be about $\ln 12$. This supposition agrees with the structural data. The Pb atoms, which have 12 local disorder positions in a cubic phase, are slightly displaced in the orthorhombic phase along the [010]_p direction of the pseudocubic cell [1]. This means that, in the latter phase, Pb atoms have two or four disordered positions leading to entropy changes $R \ln 12/2 = R \ln 6$ and $R \ln 12/4 = R \ln 3$, respectively.

5. Conclusions

Heat capacity measurements on PMW and PCW performed by means of adiabatic calorimetry have allowed us to determine the latent heat, the hysteresis of PT temperature and the total entropy change associated with structural transformations. No additional PT, as was postulated in [2, 10], was found in PMW.

Pressure measurements have shown that phase boundaries in the *p*–*T* diagrams of PMW and PCW are significantly nonlinear. The possibility of combining both phase diagrams is discussed.

The comparison of thermodynamic data with the results of structural [1, 5], Raman [9, 10] and neutron [24] studies allows us to assume that in both compounds PT from the cubic phase is connected to simultaneous partial ordering of Pb atoms and displacement of O atoms.

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