LATTICE DYNAMICS
AND PHASE TRANSITIONS

Heat Capacity and the p–T Phase Diagram of Pb_2MgTeO_6 Elpasolite

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Abstract—The heat capacity of Pb_2MgTeO_6 is measured in the temperature range 80–300 K. It is found that the heat capacity exhibits an anomaly associated with the phase transition at $T_0 = 186.9$ K. The thermodynamic parameters of the structural transformation are determined. The effect of hydrostatic pressure up to 0.5 GPa on the phase transition temperature is examined. © *2001 MAIK "Nauka/Interperiodica".*

1. INTRODUCTION

Oxygen-containing compounds with a perovskite structure ABO_3 ($Pm\bar{3}m$, $Z = 1$) are usually considered model objects owing to the great diversity of their physical properties and the relatively simple structure of their crystal lattice. The specific feature of perovskites is the striking flexibility of their structure, which makes it possible to change their atomic composition over a wide range and, thus, to achieve the desirable properties of materials. One possible way of affecting their properties is to replace the B cation by two different cations B' and B". At certain ratios between ionic radii and charges, the cations can undergo an ordering with the formation of an elpasolite structure (ordered perovskite) $A_2B'B"O_6$ ($Fm\bar{3}m$, $Z = 4$). A change in the degree of ordering of the B' and B" cations can substantially affect the physical properties of compounds and the nature of their structural transformations. The compositionally disordered (partly or completely) compounds are relaxors; i.e., they undergo diffuse (smeared) phase transitions and exhibit a dispersion of permittivity. Conversely, the ordered compounds undergo sharp phase transitions with a decrease in the temperature.

Despite extensive investigations of these compounds by different methods, many fundamental problems still remain unsolved. For all these compounds, the symmetry of distorted phases and even their number, as well as the mechanism of phase transitions, have been debated in the literature up to now. Particular attention has been concentrated on a large family of lead-containing compounds $Pb_2B'B"O_6$, among which are different-type relaxors and compositionally ordered perovskites.

The Pb_2MgTeO_6 compound was first studied in [1, 2]. The dielectric measurements performed by Politova and Venevtsev [2] revealed a small anomaly in $\varepsilon(T)$ near 190 K. The first-order phase transition at this temperature was confirmed by the structural investigations carried out by Baldinozzi *et al.* [3]. Apart from the anomaly observed at ~190 K, a small change in the permittivity was found at 145 K in [4]. Some parameters of the Raman spectra also exhibited an anomalous behavior in the temperature range 150–142 K. It should be noted that this feature was observed only in measurements upon cooling.

Baldinozzi *et al.* [4, 5] proved that the low-temperature phases are the incommensurate phases with the modulation vector $(\delta\delta\delta)$, where δ is close to 0.107 at 8 K. Analysis of the experimental data allowed these authors to make the conclusion that the phase transformation at 190 K is an improper ferroelastic transition. A trigonal ferroelastic distortion arises as a secondary order parameter upon mode condensation at an incommensurate point of the Brillouin zone. The intermediate and low-temperature phases have the $R\bar{3}m(\delta\delta\delta)$ and $R\bar{3}(\delta\delta\delta)$ symmetries, respectively.

The phase transition to the incommensurate phase is a fairly rare phenomenon in mixed oxygen-containing perovskites. Only three representatives of this family with the aforementioned transitions, namely, Pb_2CoWO_6 [6, 7], Pb_2CdWO_6 [8], and $PbSc_{1/2}Ta_{1/2}O_3$ [9], are known to date. The characteristic feature of the Pb_2MgTeO_6 compound is an extremely wide stability range of the incommensurate phase. No transitions to the commensurate phase was found down to 6 K [3, 4].

Another feature of the Pb_2MgTeO_6 compound is a rather unusual temperature behavior of the thermal ellipsoid parameters for lead ions. According to structural investigations, the $Pb_2B'B"O_6$ compounds are characterized by a high degree of positional disordering of lead ions in the initial cubic phase. For a number of

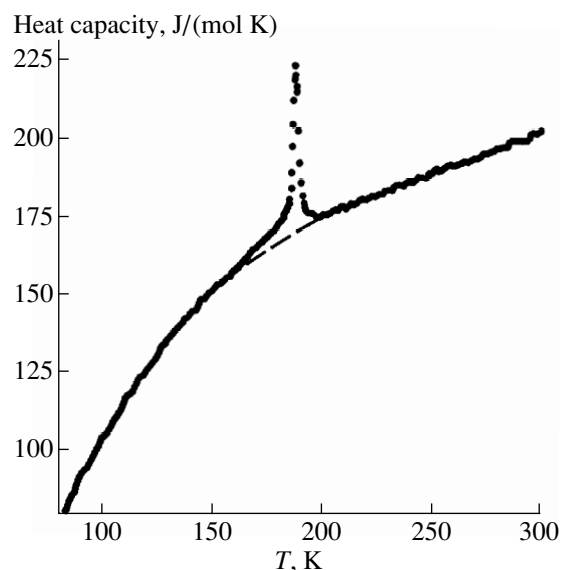**Fig. 1.** Temperature dependence of the heat capacity of Pb_2MgTeO_6. The dashed line represents the lattice heat capacity.

compounds (Pb_2CoWO_6 [10], Pb_2MgWO_6 [11], and Pb_2CdWO_6 [8]), the thermal ellipsoid parameters of lead ions become normal in the distorted phases, which suggests the ordering of lead ions. For other elpasolites, specifically for Pb_2MgTeO_6 [5], these parameters remain anomalously large. Moreover, soft modes were revealed in all these compounds. At present, the ordering processes, soft modes, and their interaction upon successive structural transformations in ordered perovskites have been studied intensively.

In the present work, we thoroughly investigated the *p–T* phase diagram and the heat capacity of the Pb_2MgTeO_6 compound over a wide range of temperatures. The purpose of this work was to determine the thermodynamic parameters of the phase transitions and to elucidate the role of the ordering processes in two groups of oxygen- and lead-containing elpasolites, which differ in the behavior of the thermal ellipsoid parameters of lead ions. It is this heat capacity that can provide reliable information on phase transitions, irrespective of their nature and mechanisms. At the same time, the data on the thermodynamic characteristics of the phase transitions (enthalpies and entropies) are required in the refinement of different models for structural transformations. In turn, analysis of the *p–T* phase diagrams enables one to gain a better insight into the interrelation between successive structural distortions in different representatives of the family under consideration.

2. EXPERIMENTAL TECHNIQUE

The powder samples to be studied were prepared by solid-phase synthesis from a stoichiometric mixture of initial oxides [3] and were used earlier in structural and Raman studies [4, 5]. Analysis of x-ray diffraction patterns showed that the sample contains a minor amount of Pb_3TeO_6 and $PbTeO_3$ impurities. No indications of the composition disordering of Mg and Te ions was found.

The heat capacity was measured using an adiabatic calorimeter in the temperature range 80–300 K. A powder sample (4.25 g) was placed in an indium cell and was sealed in a helium atmosphere. The heat capacity of the cell was measured in a separate experiment. The measurements were carried out upon continuous and discrete heating. In their immediate vicinity, the phase transitions were investigated by the quasi-static thermogram method at the mean rates of temperature change $|dT/dt| \approx (1–1.5) \times 10^{-2}$ K/min.

The effect of hydrostatic pressure on the phase transition temperature was studied with the same sample as was used in the calorimetric measurements. The change in the phase transition temperature was determined by differential thermal analysis with the use of a copper–germanium thermocouple. A quartz reference sample was placed on one junction of the thermocouple, and a small copper vessel (~0.05 cm³) with the studied compound in it was placed on another junction of the thermocouple. The high sensitivity of the thermocouple made it possible to measure the phase transitions with a small change in the enthalpy. A pressure as high as 0.5 GPa was produced in a chamber of the cylinder–piston type, which was connected to a booster. A mixture of a silicone oil and pentane was used as a pressure transmitting medium. The pressure was measured by a manganin resistance pressure gauge, and the temperature was measured using a copper–constantan thermocouple. The errors of measurements were equal to $\pm 10^{-3}$ GPa and ± 0.3 K, respectively.

3. RESULTS

The results of our measurements of the heat capacity $C_p(T)$ are displayed in Fig. 1. It is seen that $C_p(T)$ exhibits only one anomaly with a maximum at $T_0 = 187.1 \pm 0.5$ K. Figure 2 shows the experimental data on the heat capacity in the temperature range in which, according to Baldinozzi *et al.* [4], specific features in the behavior of the permittivity and the Raman spectrum parameters are observed as a result of the second phase transition. The measurements were performed upon heating and cooling. In experiments upon cooling, the sample was preliminarily heated above 190 K, i.e., above the temperature of the transition from the cubic phase. A relatively small, regular scatter of the experimental points with respect to the smoothed curve $C_p(T)$ upon both heating and cooling indicates that any anomaly in the heat capacity of the studied sample in the temperature range 133–147 K is absent, to within about 0.5% of the total heat capacity of the sample.
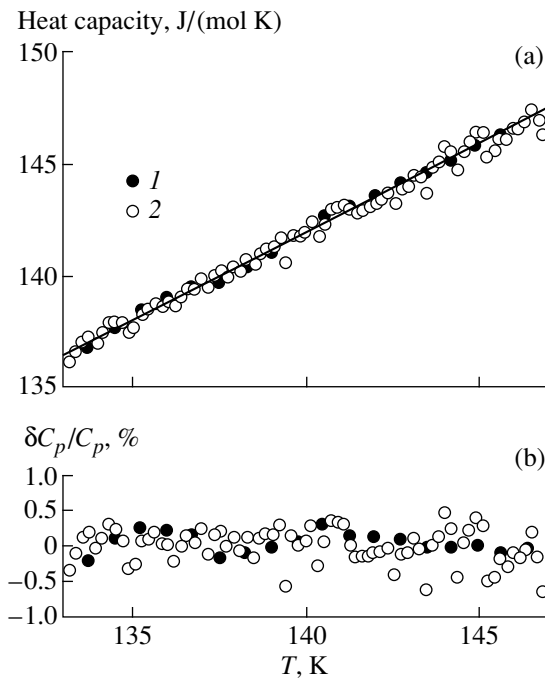
Heat capacity, J/(mol K)

Fig. 2. (a) Temperature dependences of the heat capacity measured upon continuous and discrete heating of Pb_2MgTeO_6 in the range of the second phase transition assumed in [9] and (b) deviations of the experimental points from the smoothed dependences: (*1*) heating and (*2*) cooling.

Thermographic investigations in the vicinity of the phase transition allowed us to refine the transition temperature $T_0 = 186.9 \pm 0.1$ K and to determine its hysteresis $\delta T_0 = 0.63 \pm 0.05$ K. The experimental heat capacities measured using a continuous heating technique upon heating and cooling in the phase transition range are displayed in Fig. 3. The anomaly observed in the heat capacity is strongly asymmetric. Note that the heat capacity decreases considerably more slowly in the
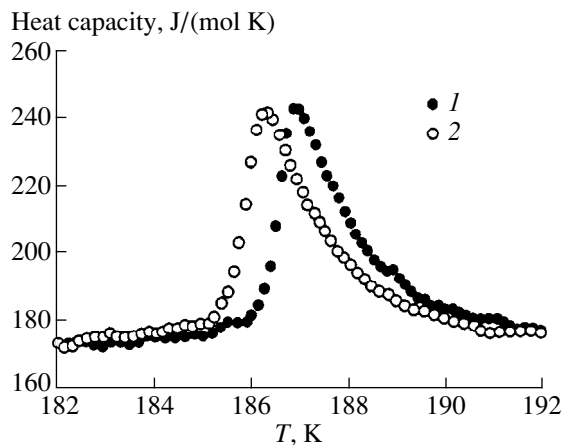
temperature range above the phase transition. As follows from the thermographic data, the latent heat of the phase transition has a small value ($\delta H_0 = 200 \pm 10$ J/mol). The corresponding change in the entropy is $\delta S_0 = \delta H_0/T_0 \cong$ 1.1 J/(mol K). A slight difference between the phase transition temperature and the temperature reported in the literature can be associated with difficulties in its accurate determination from the data of dielectric measurements and a high rate of change in temperature dT/dt in these experiments [4].

The integrated thermodynamic characteristics of the phase transition were obtained in processing the anomalous contribution of the heat capacity $\Delta C_p(T) = C_p(T) - C_l(T)$. The lattice heat capacity $C_l(T)$ was determined by the approximation of the experimental data far from the phase transition temperature with the use of the Debye and Einstein functions. The temperature dependence of the lattice heat capacity is shown by the dashed line in Fig. 1. The heat capacity anomaly is observed in a rather wide range of temperatures (from 130 to 230 K). The entropy of the phase transition was calculated by integration of the $\Delta C_p(T)/T$ function. The temperature dependence of the entropy of phase transition is displayed in Fig. 4. The total entropy change ΔS_0 is equal to 2.59 $\pm$ 0.25 J/(mol K). The ratio $\delta S_0/\Delta S_0 \approx$ 0.42 indicates that the phase transition is the first-order transformation close enough to a tricritical point.

Figure 5 shows the *p–T* phase diagram of Pb_2MgTeO_6. No anomalies that could be assigned to the pressure-induced transitions (except for the transition from the cubic phase) were found in the pressure range covered. The phase boundary is described by the linear dependence $T(p) = a + bp$ with the coefficients $a = 186.9 \pm 0.1$ K and $b = -6.07 \pm 0.10$ K/GPa.
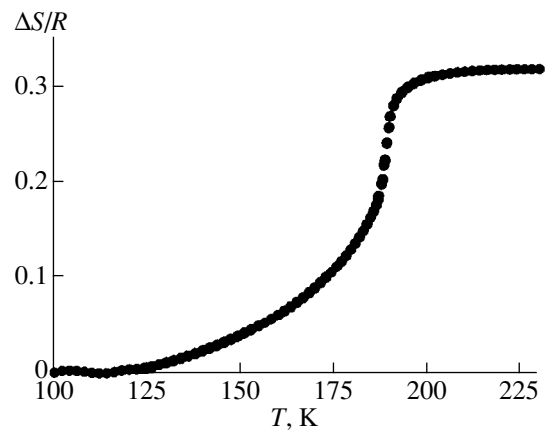

Fig. 3. Temperature dependences of the heat capacity measured upon (*1*) heating and (*2*) cooling in the vicinity of the phase transition in Pb_2MgTeO_6.

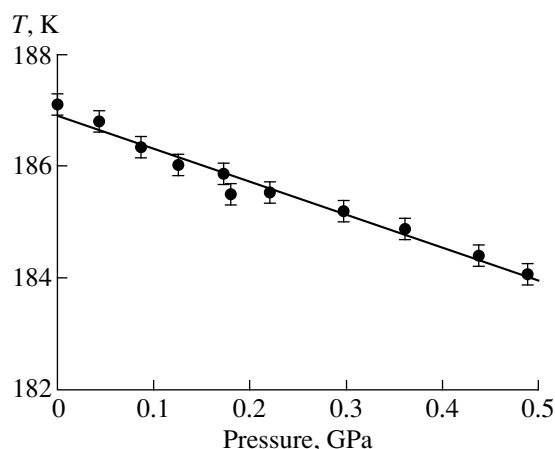**Fig. 4.** Temperature dependence of the entropy of phase transition in Pb_2MgTeO_6.

T, K

Fig. 5. The p–T phase diagram for Pb₂MgTeO₆.

4. DISCUSSION AND CONCLUSIONS

The main thermodynamic characteristics of the phase transitions in Pb_2MgTeO_6 and two oxygen-containing ordered perovskites studied in our earlier works [12, 13] are listed in the table. It is seen that the entropy change upon the phase transition in Pb_2MgTeO_6 is substantially less than the quantity ΔS for the other studied compounds. In order to elucidate the reasons for this difference, we will consider the structural characteristics of the cubic and distorted phases in these compounds.

The cubic phase in Pb_2MgTeO_6, as well as in the other representatives of this family, is characterized by a high degree of positional disordering of lead ions [10, 11]. The refinement of the structure of the $Fm\bar{3}m$ phase in Pb_2MgWO_6 and Pb_2CoWO_6, in the case when the lead ions have only one position and occupy only the $8c$

Structural and thermodynamic characteristics of phase transitions in $Pb_2B'B''O_6$ ordered perovskites

Characteristic	Pb_2MgWO_6	Pb_2CoWO_6	Pb_2MgTeO_6
T_1, K	312.8 ± 0.2	302.7 ± 0.5	186.9 ± 0.1
G_1	$Pmcn$	Incommen-surate	$R\bar{3}(\delta\delta\delta)$
δT_1, K	2.45 ± 0.2	~ 1	0.63 ± 0.05
dT_1/dp, K GPa^{-1}	-32.8 ± 1.5	37.4 ± 5.0	-6.07 ± 0.10
$\Delta S_1/R$	1.69 ± 0.14	1.15 ± 0.18	0.31 ± 0.03
T_2, K		256.2 ± 0.5	
G_2		$Pmcn$	
δT_2, K		11.4	
dT_2/dp, K GPa^{-1}		-220 ± 38	
$\Delta S_2/R$		0.18 ± 0.02	
Reference	[11, 12, 13]	[7, 13]	[4, 5], this work

sites, leads to large values of the thermal vibration parameters and the R factors. The best R factors are obtained for the case when the lead ions move in a multiple-well potential and occupy 12 equivalent positions [10, 11]. Unfortunately, the available experimental data were insufficient to perform a similar analysis for Pb_2MgTeO_6 [5]. Nonetheless, the large thermal parameter suggests that lead ions in this compound are also displaced from the $8c$ positions and disordered.

In Pb_2MgWO_6 and Pb_2CoWO_6, the phase transitions bring about the ordering of the lead atoms. In Pb_2MgTeO_6, the thermal parameters of lead ions remain anomalously large with a decrease in the temperature, which indicates that the lead ions remain disordered in the low-temperature distorted phase [5]. A similar situation is also observed in $PbFe_{0.5}Nb_{0.5}O_3$ [14], $PbSc_{0.5}Nb_{0.5}O_3$ [15], and $PbFe_{0.5}Ta_{0.5}O_3$ [16].

In the cubic phases of all the aforementioned compounds, the thermal parameters of oxygen ions are also rather large. As the phase transition temperature is approached upon cooling, the thermal ellipsoid for the oxygen ions becomes increasingly flattened, which was attributed [5] to the softening of the modes responsible for the phase transition.

As regards the structural features associated with the lead ions, it seems likely that there exists a difference between the compounds in which the main distortion is rhombohedral and those in which it is pseudotetragonal. In the latter compounds, no positional disordering of the lead ions is observed in the low-temperature phase. Actually, in Pb_2MgWO_6 and Pb_2CoWO_6, the large thermal ellipsoid parameters for the lead ions in the cubic phase become normal below the phase transition temperatures [11]. The significant role of the lead ordering in the mechanism of phase transitions is also confirmed by the results of calorimetric investigations of these compounds [12, 13]: the entropy change is $\Delta S/R \approx \ln 4 - \ln 6$.

One reason for this behavior of the lead ions can be their tendency toward the formation of tetrahedral coordination polyhedra PbO_4 [17]. These polyhedra were found in the pseudotetragonal low-temperature phase of Pb_2MgWO_6 [11]. In the case of rhombohedral symmetry, the ordering of the lead ions on a threefold axis can result only in the PbO_3 configuration. The PbO_4 configuration can be realized in this symmetry when the lead ions are displaced from the threefold axis and are disordered over several positions. The absence of a substantial change in the positional disordering of lead ions upon phase transition in Pb_2MgTeO_6 is supported by the entropy change $\Delta S/R = 0.31$, which was obtained in the present work.

The parameters of the p–T phase diagrams for the compounds under considerations (see table) are also noteworthy. The substantial difference in the values of dT_1/dp stands out. In this respect, it is necessary to return to the question about the existence of the second

phase transition in Pb_2MgWO_6. As was noted in our earlier work [13], the *p–T* diagrams for the Pb_2MgWO_6 and Pb_2CoWO_6 compounds can be treated as related. To put it differently, the line of the phase transition $Fm\bar{3}m \longrightarrow Pmcn$ in the magnesium compound is split when the unit cell volume changes and the intermediate incommensurate phase is formed in cobalt elpasolite. In our opinion, this is the main reason why both the magnitudes of dT_1/dp and their signs differ for these elpasolites. A small shift in T_1 under a pressure in Pb_2MgTeO_6 counts in favor of the difference in the mechanism of phase transition in this compound, which is in agreement with the data of structural and calorimetric investigations. As regards the second phase transition in this compound, the question remains open.

ACKNOWLEDGMENTS

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