The mineral mayenite was discovered in 1964 [1]. It is the natural modification of the mixed oxide 12CaO ⋅ 7Al2O3 (C12A7), which was already known in materials science at that time. A specific feature of the mayenite structure is that it consists of a rigid \((\text{Ca}_{12}\text{Al}_{14}\text{O}_{32})^{2+}\) framework and weakly bound \(\text{O}^{2-}\) anions on energetically equivalent sites, whose occupancy is \(1/6\) [2]. For this reason, mayenite is referred to as an antizeolite material [3, 4]. It was demonstrated that mayenite has oxygen ion conductivity due to the weakly bound anions [5]. Another specific feature of this structure is the presence of closed nanosized cages [6], so mayenite can be regarded as having intrinsic nanosized porosity. Although solid electrolytes with a large inner surface area are of great interest as a new class of compounds, there has been no systematic investigation of these systems. The melting point of mayenite is estimated 1633 to 1728 K in different publications [7–12]. A transition between two cubic phases was hypothesized to take place in mayenite at 1310 ± 10 K [13]. Here, we report a further investigation of phase transitions in \((\text{Ca}_{12}\text{Al}_{14}\text{O}_{32})^{2+}\).

**EXPERIMENTAL**

The synthesis of mayenite \((\text{Ca}_{12}\text{Al}_{14}\text{O}_{32})^{2+}\) was described in our earlier publication [14]. The starting chemicals for the solid-phase synthesis of mayenite were \(\gamma\)-\(\text{Al}_{2}\text{O}_{3}\) (analytical grade) and \(\text{CaCO}_{3}\) (pure grade). The resulting material was proved to be a single phase by X-ray diffraction and Raman spectroscopy [14]. It has a cubic structure with a unit cell parameter of \(a = 11.987\) Å at room temperature.

X-ray diffraction patterns were obtained on a Rigaku DMAX-2200/PC diffractometer (CuKα radiation) with a high-temperature attachment. The sample holder and sample heater were made from platinum. Because of this, the diffraction patterns showed reflections both from the sample and from platinum.

The thermal behavior of mayenite was studied by differential scanning calorimetry (DSC) and thermogravimetry (TG) on an STA 449C Jupiter® synchronous thermal analyzer (Netzsch, Germany). The heating rate was 9.8 K/min.

Dilatometric studies were carried out in air on a Netzsch 402C automated dilatometer. The temperature ramp rate was varied between 1 and 5 K/min.

**RESULTS AND DISCUSSION**

**Synchronous TG–DSC Analysis**

Figure 1 shows the TG curve for the first heating of mayenite in air (M). The curve indicates two weight loss stages and can be represented as the sum of the partial curves M1 and M2, which were obtained by fitting two portions of the experimental curve to the Boltzmann function. In the second heating cycle, no change in the sample weight is detected at moderate temperatures. At high temperatures, a slight weight loss is observed even in the second and third heating cycles. The weight loss of mayenite between 473 and 773 K (temperature range covered by the partial curve M1) was reported by Nurse et al. [8]. The weight change at higher temperatures (indicated by the partial curve M2) is in agreement with data of Hayashi et al. [15] and can be interpreted in terms of water vapor exchange between the sample and the gas phase.

Figure 2 presents DSC data for mayenite. We believe that the endothermic event beginning near
1650 K is the melting of the sample. Most of the relevant publications (e.g., [7–12, 16–18]) deal with temperatures near the melting point and above. The melting point of mayenite is estimated by different authors at 1633 K [7] to 1728 K [12]. This wide spread of melting point data is attributed to the fact that the sample sorbs water and thus changes its composition.

The melting point of mayenite has not been precisely determined, because of the following circumstances. In DSC, the temperature of a thermal event is measured as its onset temperature, more specifically, the intersection point between the tangents to two DSC curve segments, one belonging to the base line and the other to the peak front. In DTA, the temperature of an event is recorded as the peak temperature, which is somewhat higher than the temperature determined by DSC. According to our data, the onset temperature of melting of the initial mayenite sample (1647.1 K) differs from the same temperature measured in the second thermal cycle (after dehydration), in which the sample does not change its weight (1626.3 K). Thus, our melting point data are in good agreement with the literature.

We have found only two reports on the thermal behavior of the solid phase of Ca$_{12}$Al$_{14}$O$_{33}$ [8, 13].

In Fig. 2a, the derivatives of the TG curves M1 and M2 with respect to temperature are superimposed on the first-cycle DSC curve. As is clear from Fig. 2a, the DSC curve indicates two thermal events characterized by the largest weight loss, namely, an exotherm at ~600 K and an endotherm at 1100 to 1400 K (depending on the sample history).

We think that the process taking place at 600 K is the dehydration of the material. According to our estimates, it is near this temperature that the relative stabilities of the Ca–O and Ca–OH bonds change. Calcium oxide is stable at high temperatures; calcium hydroxide, at lower temperatures. The dehydration process is exothermic (Fig. 2a).

Figure 2b presents the DSC curve (Fig. 2a) processed using standard software (NETZSCH Peak Separation). This approach makes it possible to separate the dehydration peak and to exclude the dehydration process from consideration.

Figure 2c shows the DSC curves recorded in the second and third cycles up to a temperature of 1373 K, until the release of strongly bound water. The curve indicates a reproducible exotherm. As will be demonstrated below, this exotherm arises from a phase transition. The enthalpy of this phase transition is $-277 \pm 20$ J/g. The molar mass of mayenite is 1386.681 g/mol. Therefore, the enthalpy of the phase transition in systematic units is $-384 \pm 28$ kJ/mol. With the transition temperature (898 ± 25 K) taken into account, the change in the entropy of the material is $-428 \pm 32$ J/(mol K).

The endothermic peak observed as the temperature is further raised is actually a doublet (Fig. 2d). Note that the opinion that mayenite is an oxyhydroxide [15] provides an explanation for the doublet character of this endothermic peak and for the corresponding weight change. The latter is tentatively attributed to the release of water via the reaction

$$2(OH)^- = O^{2-} + H_2O.$$  

Weakly bound oxygen, which is a specific feature of the mayenite phase, reacts readily with water to yield hydroxide groups. Therefore, mayenite is always an oxyhydroxide, with the O/OH ratio depending on the sample synthesis and storage conditions and history. It was reported that mayenite has a heat capacity peak at 1310 K [13].

**Dilatometric Study of the Phase Transition**

Dilatometric studies were performed in a temperature range in which the sample did not change its composition (between the extremums of the derivatives of the partial TG curves shown in Fig. 2a). Measurements were taken both from a ceramic mayenite sample obtained in a standard way [14] (~20% porosity) and from a dense ceramic sample whose preparation is described in [19]. The heating rate was 1, 2.5, or 5 K/min. The data obtained in the first cycle were excluded from data processing. There is a point at which the relative extension versus temperature curve changes its slope (Fig. 3a). This shape of the curve indicates a second-order phase transition.

The primary dilatometric data were processed by the difference method [20–22]: experimental data were fitted to a straight line and the data represented by this line were subtracted from the experimental data. This data processing method makes it possible to enhance the accuracy of determination of the temperature at which the extension versus temperature curve changes its slope or has a discontinuity and to identify the type of phase transition more clearly. The resulting difference as a function of temperature has an extremum (Fig. 3b), not a discontinuity, indicating that the