

Conductivity and phase transitions in a potassium–magnesium molybdate

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The potassium–magnesium molybdate $\text{K}_2\text{Mg}_2(\text{MoO}_4)_3$ shows a two-step phase transition associated with the sharp appearance of a potassium motion leading to highly conductive properties above the phase transition temperature.

Alkali metals with large radii (K, Rb and Cs) are characterised by low mobility in inorganic materials.^{1,2} Materials with the NASICON structure $[\text{M}^{\text{I}}\text{M}_2^{\text{V}}(\text{PO}_4)_3]$ can be considered a good conductive matrix for these ions due to the presence of wide channels in which ions can move easily.¹ The NASICON framework is built up of $\text{M}^{\text{IV}}\text{O}_6$ octahedra and PO_4 tetrahedra sharing corners. $\text{K}_2\text{Mg}_2(\text{MoO}_4)_3$ with an analogous structure undergoes a monoclinic-rhombohedral phase transition³ at about 510 °C.

The purpose of this work was to study phase transitions and ion conductivity in a potassium–magnesium molybdate $[\text{K}_2\text{Mg}_2(\text{MoO}_4)_3]$ and related materials doped with scandium(III) or vanadium(V) ions.

According to X-ray diffraction data, at room temperature, $\text{K}_2\text{Mg}_2(\text{MoO}_4)_3$ ceramics obtained at 480 and 700 °C are high-temperature phases despite the fact that in the former case the synthesis temperature was below the phase transition temperature.³ At the same time, the material standing within a year at room temperature leads to its transition into a low-temperature phase. The X-ray diffraction patterns of this material obtained on heating (Figure 1) show that the low-temperature phase transforms to a high-temperature form above 490 °C. However, after cooling the X-ray diffraction pattern of this phase is restored only after long standing at room temperature.

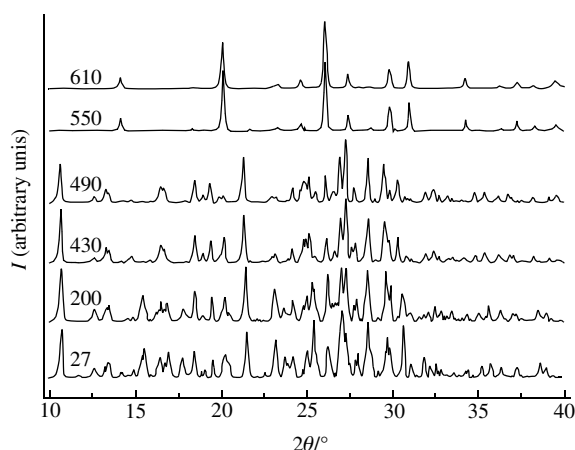


Figure 1 Portions of X-ray diffraction patterns for $\text{K}_2\text{Mg}_2(\text{MoO}_4)_3$ in the temperature range 27–510 °C.

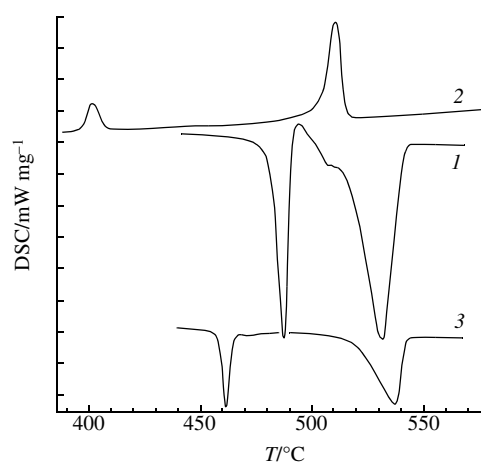


Figure 2 DTA curves for $\text{K}_2\text{Mg}_2(\text{MoO}_4)_3$: (1) the first heating, (2) cooling and (3) the second heating.

The X-ray diffraction patterns of molybdates doped with scandium and vanadium have reflections similar to those of $\text{K}_2\text{Mg}_2(\text{MoO}_4)_3$. Lattice parameters of all obtained materials are close to those for high-temperature $\text{K}_2\text{Mg}_2(\text{MoO}_4)_3$; this suggests a solid solution formation.

In order to study phase transitions in $\text{K}_2\text{Mg}_2(\text{MoO}_4)_3$, differential thermal analysis (DTA) was carried out in a cyclic heating cooling regime in the temperature range 420–580 °C. Two endo peaks with maxima at 489 and 535 °C were observed during the first heating. The heats of transition are 26 and 62 J g^{−1}, respectively. At the same time, during the subsequent heating, such transformations occur at 464±1 and 538±1 °C with the heats of transition of 5.5±0.6 and 15.5±1.0 J g^{−1} respectively. On cooling, two exo peaks were observed at 510±1 and 403±2 °C with essentially smaller heats. The presence of a high-temperature phase in the material kept for a short time at a low temperature after cooling decreases the temperature of the first stage and catalyses $\text{K}_2\text{Mg}_2(\text{MoO}_4)_3$ transition to a high-temperature phase on heating. Thus, the X-ray diffraction and DTA data allow us to conclude that $\text{K}_2\text{Mg}_2(\text{MoO}_4)_3$ undergoes the ‘broken’ phase transition.

The temperature dependence of the ion conductivity of $\text{K}_2\text{Mg}_2(\text{MoO}_4)_3$ is shown in Figure 3. Below 280 °C, the conductivity is low and the data are not quite reliable. However, above this temperature, the conductivity gradually increases up to 2.5×10^{−5} S cm^{−1} at 530 °C. The further heating results in a sharp increase in the conductivity by two orders of magnitude.

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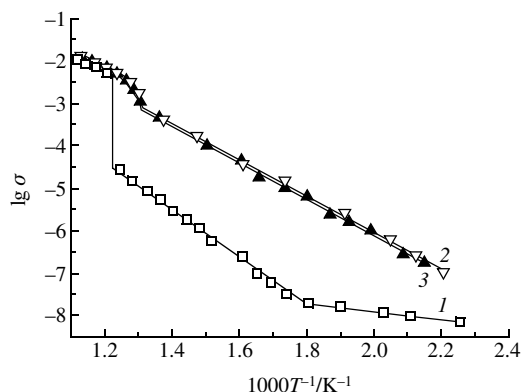


Figure 3 Temperature dependence of $K_2Mg_2(MoO_4)_3$ conductivity: (1) the first heating, (2) cooling and (3) the second heating.

This increase in the conductivity is usually attributed to a superionic phase transition. In the case of $K_2Mg_2(MoO_4)_3$, it is due to potassium ions disorder. The transition temperature correlates with DTA and X-ray diffraction data. At 620 °C, the conductivity is equal to $10^{-2} \text{ S cm}^{-1}$. This value is very high for potassium ions. A similar sharp conductivity decrease was not found on material cooling. The conductivity decreases smoothly with an activation energy of about 60 kJ mol^{-1} in this temperature range. A conductivity change by half-order of magnitude was found only in the temperature range of 460–490 °C. During the following heating right after cooling or in some days the temperature dependence of the conductivity is similar to that obtained on cooling.

Aliovalent doping usually results in an increase in the cation mobility and a decrease in the phase transition temperature. From this point of view, the stabilization of highly conductive phases by the aliovalent doping of $K_2Mg_2(MoO_4)_3$ seems very attractive.²

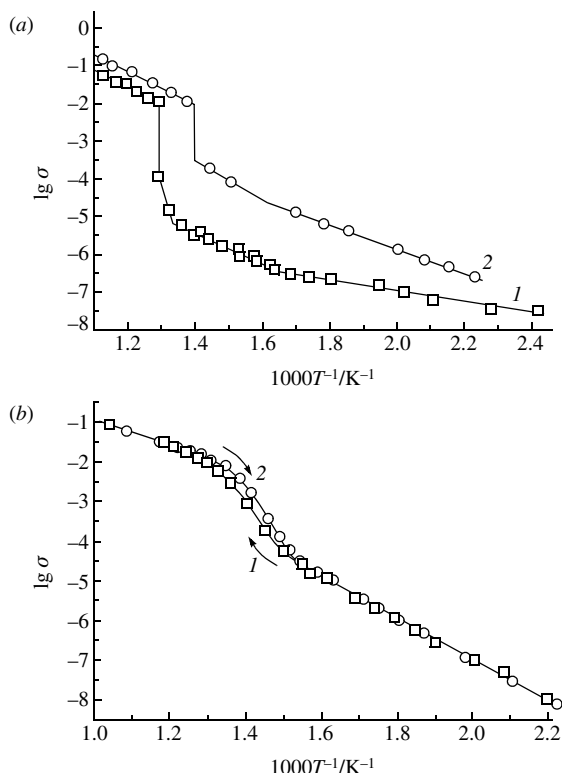


Figure 4 Temperature dependence of (a) $K_{1.99}Mg_{1.99}Sc_{0.01}(MoO_4)_3$ conductivity: (1) heating and (2) cooling; (b) $K_{2.03}Mg_2(Mo_{0.99}V_{0.01}O_4)_3$ conductivity: (1) heating and (2) cooling.

The replacement of magnesium ions by scandium in $K_2Mg_2(MoO_4)_3$ is accompanied by potassium vacancy formation $[K_{1.99}\square_{0.01}Mg_{1.99}Sc_{0.01}(MoO_4)_3]$, where the symbol \square denotes a vacancy in potassium positions. This substitution results in an insignificant conductivity increase in the low-temperatures range [Figure 4(a)]. The conductivity of $K_{1.99}\square_{0.01}Mg_{1.99}Sc_{0.01}(MoO_4)_3$ is higher than that of $K_2Mg_2(MoO_4)_3$ after phase transition temperature. However, on cooling, the conductivity of $K_{1.99}\square_{0.01}Mg_{1.99}Sc_{0.01}(MoO_4)_3$ decreases in a similar manner for the undoped material.

The replacement of molybdenum by vanadium, on the contrary, is accompanied by the introduction of additional potassium ions into interstitials $[K_2(K_i)_{0.03}Mg_2(Mo_{0.99}V_{0.01}O_4)_3]$, where the symbol K_i denotes potassium ions in interstitials. In this case, the conductivity of the low-temperature modification of $K_2(K_i)_{0.03}Mg_2(Mo_{0.99}V_{0.01}O_4)_3$ is higher than that of $K_2Mg_2(MoO_4)_3$. The increase in conductivity caused by a phase transition was observed in the temperature range of 400–510 °C. However, the increase in the conductivity is smaller in comparison with the previous materials, as well as the ‘hysteresis loop’ during a heating–cooling cycle [Figure 4(b)].

It well correlates with the DTA data on an essentially smaller value of the *endo* effects corresponding to a superionic phase transition. The changes of DTA curves for the modified sample of $K_2(K_i)_{0.03}Mg_2(Mo_{0.99}V_{0.01}O_4)_3$ are similar to those for $K_2Mg_2(MoO_4)_3$. However, phase transition temperatures and *endo* effect values are lower. On the first heating, two *endo* effects with maxima at 476 and 516 °C and transition heats of 2.6 and 9 J g^{-1} were found. On cooling, the maxima of these effects are shifted to 473 ± 2 and 391 ± 2 °C, respectively. The heat of the second one decreased to $3.9 \pm 0.1 \text{ J g}^{-1}$, while for the first remains almost constant ($2.7 \pm 0.1 \text{ J g}^{-1}$). During the following heating, the transition temperatures are equal to 470 ± 1 and 504 ± 1 °C. The total value of *endo* effects is four times lower than that of the undoped material. It results in a small hysteresis loop on the temperature dependence of conductivity. The X-ray diffraction pattern of $K_2(K_i)_{0.03}Mg_2(Mo_{0.99}V_{0.01}O_4)_3$ slightly varied on heating. It is possible to note only the disappearance of some weak reflections above 490 °C. Thus, the structure transformation on heating is much smaller. The above facts testify that potassium transfer by interstitials dominates in the low-temperature phase.

Potassium–magnesium molybdates can be considered as promising solid electrolytes due to the observed high potassium conductivity. Conductivity can be increased by aliovalent doping. The mobility of potassium interstitials exceeds vacancy mobility.

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