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Anelastic and dielectric studies of $La_2Mo_2O_9$-based oxide-ion conductors

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Abstract

This paper reports the results of internal friction and dielectric relaxation studies on novel oxide-ion conductors $(La_{1-x}A_x)_2Mo_2O_{9-\delta}$ (A = Ca, Bi, K; x = 0–0.075). Two relaxation peaks associated with short-distance diffusion of oxygen vacancies were observed. Doping at La site with different elements shifts both relaxation peaks towards higher temperature and increases the activation energy of oxygen ion diffusion. In the case of internal friction, the height of the higher temperature peak (dominant component) decreases with increasing dopant content, while the lower temperature peak increases slightly. In the case of dielectric relaxation, on the other hand, the variation of the peak heights as a function of doping content exhibits a maximum around 2.5% K and 4% Bi. Furthermore, in undoped and slightly doped $La_2Mo_2O_9$ samples, there is an internal friction peak around 570 °C associated with the order–disorder phase transition. In heavily doped samples, this peak disappears, indicating that this phase transition is suppressed and the high temperature phase is stabilized.

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Keywords: Oxide-ion conductor; Internal friction; Dielectric relaxation; $La_2Mo_2O_9$

1. Introduction

Oxide-ion conductors have been receiving widespread interest because of their potential applications in solid oxide fuel cells (SOFC), oxygen sensors, oxygen pumps and oxygen-permeable membrane catalysts [1–4]. In most of these applications the working temperature is usually high enough to achieve a relatively great oxygen flux for efficient operation if traditional oxide-ion conductors are used, which include the doped perovskite-type ionic oxide [1,5], yttria-stabilized zirconia (YSZ) [4,6–8] and pyrochlore compounds [9]. Concerning with the practical applications, it is very important to develop materials that exhibit high oxygen ion conductivity at lower temperature. Doped ceria [10] and doped lanthanum gallate [11] are reported to have such characteristics and to be potential candidates as electrolytes of SOFC. Recently, Lacorre et al. [12,13] reported that lanthanum molybdate, $La_2Mo_2O_9$, exhibits as high ionic conductivity as 6 S/m at 800 °C. Since then, the $La_2Mo_2O_9$-based oxide-ion conductors have attracted more and more attentions [14–20]. The possible substitution of $La_2Mo_2O_9$-based oxide-ion conductors for the commonly used YSZ in SOFC application would reduce the working temperature from 1000 °C down to 800 °C, resulting in a great reduction in costs. Owing to cheap raw materials and simple synthesis process, the $La_2Mo_2O_9$-based compounds could compete with the doped ceria and doped lanthanum gallate as candidates for the electrolyte of SOFC working at intermediate temperature.

In $La_2Mo_2O_9$ compounds, the high concentration of oxygen vacancies intrinsically embedded in the crystal lattice enhances the oxygen ion diffusion and is thus considered as the essential reason for the excellent anionic conduction. In the undoped $La_2Mo_2O_9$ samples, however, there exists a first-order phase transition around 580 °C from a high temperature cubic phase (space group $P2_13$) to a low temperature monoclinic phase [12–14], resulting in a dramatic decrease of ionic conductivity at lower temperatures. At the same time, the sharp change of the lattice constant induced by this phase transition is to deteriorate the mechanical and thermal stability of devices consisting of this material. In addition, the hexavalent Mo is not stable in reducing atmosphere, resulting in an electronic conduction and even the decomposition of the compounds [21,22]. Thus, suppressing this phase transition, stabilizing the high temperature

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phase to low temperature, and improving the electrochemical stability are of great practical importance. To do this, doping at La and/or Mo sites is proved to be one of the most effective methods [22,23].

In oxide-ion conductors, point defects such as oxygen vacancies and their complexes with dopants are the abundant defects and can cause relaxational phenomena due to short-distance jumps between neighboring lattice sites. The internal friction (or mechanical spectroscopy) and dielectric relaxation are two of the most sensitive methods to investigate the dynamic process of oxygen-vacancy diffusion. In this paper, the stress is to report internal friction and dielectric relaxation investigation of the effects of doping on the oxygen-vacancy diffusion and phase transition in undoped and doped $La_2Mo_2O_9$.

2. Experimental details

The samples of $(La_{1-x}A_x)_2Mo_2O_{9-\delta}$ (A = Ca, Bi, K; x = 0–0.075) were prepared by conventional solid-state reaction from a stoichiometric mixture of La_2O_3, MoO_3, Bi_2O_3, $CaCO_3$ or K_2CO_3 powders, respectively [16]. The well-mixed powders were calcined in an alumina crucible at 623 K for 10 h in air to prevent evaporation of MoO_3, and then calcined at 1173–1223 K for 12 h with two or three times of intermediate fine grinding, and pressed into a mold to form a bar (64 mm × 4 mm × 1.5 mm) for internal friction measurements and a pellet (Ø 20 mm × 2 mm) for dielectric relaxation measurements and the direct-current (dc) conductivity measurements. These samples were finally sintered at 1223–1323 K for 12 h in air.

Low-frequency internal friction was measured on a computer-controlled torsion pendulum with the forced vibration mode at 0.5, 1, 2, and 4 Hz, respectively. All measurements are made in ascending temperature runs with a heating rate of 5 K/min and a shear strain amplitude of 2.5×10^{-5}. Before dielectric relaxation and dc conductivity measurements silver paste was deposited onto both sides of the sample as electrodes, which are connected to the experimental setup through platinum wires. The temperature spectra of dielectric relaxation were measured at various frequencies using a Hioki 3531 Z-Hitester made in Japan. This setup operates in a frequency range from 42 Hz to 5 MHz, and can measure the dielectric loss in a range from 10^{-5} to 10^{+1}.

The crystal structure of the high temperature phase of $La_2Mo_2O_9$ is cubic with space group $P2_13$. Four La ions and four Mo ions located near the eight cube-corners, while 18 oxygen ions are accommodated around them, as shown in Fig. 1. As a result, in the areas around the body-center and face-centers there is much spare space, which provides the possible paths for oxygen ion diffusion. Since 4a with 4 coordination and 12b with 12 coordination are the only available sites for space group $P2_13$, another 12b site (O(3) site) is necessary for accommodation of the extra two oxygen atoms when La, Mo, and O(1) ions occupy 4a sites and O(2) ions occupy 12b sites. As a result, 18 oxygen ions will be distributed over 28 possible sites, giving a total occupancy of 64%. However, among the ideal vacancy probability of 36%, only a fraction can take part in the process of relaxation because of the crystallographic or energetic reasons,

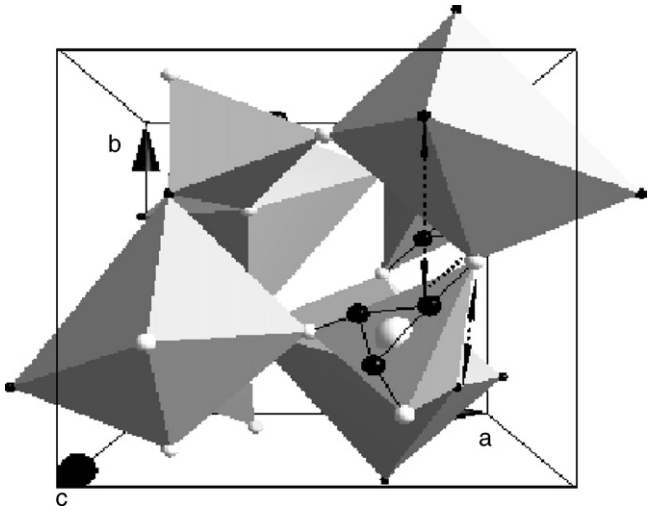

Fig. 1. The crystal structure of the high temperature cubic phase of $La_2Mo_2O_9$, where the LaO_6 octahedra and the MoO_4 tetrahedra are shown. The large and small black balls are O(3) and O(1) ions, the large and small white balls are Mo and O(2) ions, respectively. The O(2) and O(3) sites are partially occupied. The O(3) ions are not included to form MoO_7 decahedron for clarity.

and this fraction may be less in the monoclinic structure of the low temperature phase.

3. Results

3.1. Internal friction

The temperature dependence of internal friction and relative shear modulus of a undoped $La_2Mo_2O_9$ sample is shown in Fig. 2. A broad internal friction peak is observed around 400 K at 1 Hz. At a higher frequency of 4 Hz, this peak appears at a higher temperature of 420 K, as shown in the inset of Fig. 2. The peak is accompanied by strong modulus variation, i.e. the modulus decreases dramatically with increasing temperature, indicating a relaxation character of this peak. This decrease of modulus is seemingly composed of two steps centered, respectively, at about 330 and 390 K at 1 Hz, implying fine structure of this

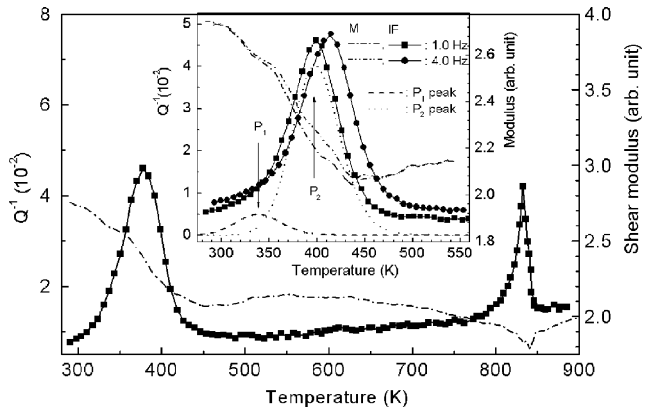

Fig. 2. Temperature dependence of the internal friction (symbols) and the relative shear modulus (lines) of an undoped $La_2Mo_2O_9$ sample. The inset shows the data at low temperature at two frequencies and the decomposition of the internal friction spectrum at f = 1 Hz into two components (P_1 and P_2).