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High-pressure dielectric behavior of polycrystalline $CaMoO_4$: The role of grain boundaries

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ABSTRACT

The dielectric behavior of polycrystalline $CaMoO_4$ was investigated at pressures up to 36.0 GPa using *in situ* impedance measurements. Grain boundaries played a dominant role in the electrical transport process. Grain boundary microstructures rearranged with the application of pressures, and the relaxation activation energy increased with increasing pressure in the tetragonal phase but decreased in the monoclinic phase. The variation of the bulk resistance with pressure was attributed to defects generated during the compression. The increasing grain boundary resistance with pressure in the tetragonal phase was caused by the increased number of dangling bonds. In the tetragonal phase, localization around O atoms weakened with increasing pressure, which promoted the polarization of Mo–O electric diploes and led to an increase of the relative dielectric constant. In addition, the dielectric loss tangent of $CaMoO_4$ was significantly reduced in the low frequency range after a pressure cycle. This work demonstrates that regulation of the polycrystalline dielectric performance by modifying the grain boundary distribution under compression can be used as an effective method to improve the bulk properties of ABO_4-type dielectrics.

1. Introduction

With increasing resource requirements, scheelite-structured molybdates have received considerable attention as a new type of functional material for a wide range of applications [1–4]. Calcium molybdate ($CaMoO_4$) is a representative example; at ambient conditions, its Ca atom exhibits eight-fold oxygen coordination, and the Mo atom forms a MoO_4^{2-} tetrahedron. This special structure endows $CaMoO_4$ with excellent properties, such as good thermal chemical stability and eminent luminescence properties, leading to its wide application in white light emitting diodes, displays, and devices in photochemical fields [5–8]. $CaMoO_4$ is also a potential candidate for microwave dielectric devices that require materials with low permittivity and high quality factors, such as dielectric resonators [9,10]. In addition, $CaMoO_4$ is an excellent host material for various rare-earth ions. By controlling the type and concentration of doped ions, the luminescent color and efficiency of $CaMoO_4$ can be modified, providing a foundation for different optical $CaMoO_4$-based applications [11,12].

In addition to doping, the external parameters of temperature and pressure also provide powerful means to tune the structure and properties of materials [13]. Previous investigations have revealed that scheelite-structured $CaMoO_4$ exhibits good structural stability at extremely high and low temperatures (6 K–1300 K) [5,6]; however, structural phase transitions occur under compression. Nicol et al. first reported an unknown pressure-induced phase transition in single crystal $CaMoO_4$ starting at 2.7 GPa based on Raman scattering for pressures up to 4 GPa [14]. However, using X-ray diffraction analysis, Hazen et al. showed that no reversible phase transitions occurred in single crystal $CaMoO_4$ up to 6 GPa and that significant structural changes occurred in the eight-coordinated site, which changed more parallel to *c* than perpendicular to *c* with changes in pressure [15]. Another room-temperature Raman scattering study of single crystal $CaMoO_4$

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was performed by Christofilos et al., and the experimental pressure was extended to 23 GPa [16]. These authors concluded that the single crystal $CaMoO_4$ underwent two phase transitions at 8.2 and 15 GPa.

Compared with single crystals, polycrystals contain many grain boundaries, and the structures and properties are affected by both the grains and grain boundaries. Hence, the pressure effects on the structural properties of polycrystals could differ. For example, using Raman experiments, Breitinger et al. observed that no phase transitions occurred in polycrystalline $CaMoO_4$ up to 3 GPa [17]. Then, combining X-ray diffraction experiments with General Structure Analysis System (GSAS) software, Crichton et al. uncovered the phase transition of polycrystalline $CaMoO_4$ from its initial tetragonal phase to a monoclinic phase at 15 GPa [18]. The structural behaviors of polycrystalline $CaMoO_4$ thus differ from those of its single crystal counterpart under compression, which is related to the grain boundary effect.

In addition to driving materials toward higher-density structures and tuning the intra- and intermolecular structures, pressure can also regulate the electrical transport properties of materials [19,20]. However, the understanding of the pressure effect on the electrical behavior of $CaMoO_4$, such as the relaxation process, complex dielectric properties, and effect of electric field and pressure on the electrical polarization and motion of bound charges, remains rather limited. Unlike their single crystalline counterparts, polycrystalline materials contain a large number of grain boundaries, which result in special properties. Grain boundaries are generally produced by some interaction between neighboring grains, which can improve the initial performance of bulk materials or even generate properties that cannot be achieved by individual grain. Therefore, the interaction of grains across a grain boundary can be a source of desirable bulk properties if the grain boundaries are properly designed and controlled. It is thus worthwhile to explore the effects of grain boundaries on the transport and dielectric properties of materials. Therefore, a systematic study of the high-pressure dielectric behavior of polycrystalline $CaMoO_4$ is necessary.

In this work, we conducted *in situ* alternate-current (AC) impedance spectra measurements in a diamond anvil cell (DAC) at pressures up to 36.0 GPa to obtain a comprehensive understanding of the dielectric behavior of polycrystalline $CaMoO_4$ under compression. The contributions of bulk and grain boundary effects on the electrical transport processes are distinguished, and the relaxation frequency, complex dielectric constant, modulus, and dielectric loss of $CaMoO_4$ under compression are also discussed. In addition, the first-principles calculations were performed to obtain a better understanding of the electronic transport behavior of $CaMoO_4$ under compression.

2. Experimental and theoretical methods

Polycrystalline $CaMoO_4$ powder was purchased from Alfa Aesar Co. with a purity of 99.9965%. The sample initially exhibited a tetragonal structure with space group $I4_1/a$, which was verified by X-ray diffraction measurements, as shown in Fig. S1 in the supplementary material. A DAC was used to conduct high pressure experiments. The impedance measurements were performed using a Solartron 1260 impedance analyzer equipped with Solartron 1296 dielectric interface. The parallel-plate electrodes configuration was selected for the AC impedance spectra measurements, and the fabrication process for the detecting microcircuit on diamond anvils is described in our previous works [21–23]. A sine voltage signal with an amplitude of 1.0 V was applied to the sample. To ensure the accuracy of the electrical measurements, no pressure transmitting medium was introduced. Ruby fluorescence was used as a pressure scale for pressure calibration [24]. The sample thickness under compression was measured with a micrometer [25].

The first-principles calculations were performed based on the density functional theory and the pseudo potential method on the standard CASTEP program in the Material Studio package [26]. The electron–ion interaction was described by Vanderbilt-type ultrasoft pseudopotentials [27]. The exchange and correlation terms were described using the generalized gradient approximation (GGA) in the scheme of Perdew–Burke–Ernzerhof (PBE) parameterization [28]. The geometric optimization of the unit cell was conducted with the Broyden–Fletcher–Goldfarb–Shanno (BFGS) minimization algorithm. Integration in the Brillouin zone was performed using special k points generated with $7 \times 7 \times 9$ and $7 \times 3 \times 7$ mesh parameter grids for the tetragonal and monoclinic phases, respectively. A plane-wave cutoff energy of 540 eV was set up for the two phases to guarantee the convergence of the enthalpy calculations.

3. Results and discussion

The Z''–Z' impedance spectra of $CaMoO_4$ under various pressures are presented in Fig. 1(a)–(c). Each spectrum includes two semicircular arcs: one is large and clear, and the another is small but visible, as shown in the insets. The left small arc represents the bulk conduction in the high frequency region, and the right large one in the low frequency region corresponds to the grain boundary conduction. The frequency dependence of the imaginary part Z''–f of $CaMoO_4$ under different pressures is shown in Fig. 1(d)–(f). The relaxation peak at low frequency corresponds to the grain boundary conduction of $CaMoO_4$. The position and intensity of the relaxation peak describe the electrical relaxation processes occurring in $CaMoO_4$. The relaxation frequency corresponds to the imaginary impedance peak and equals the reciprocal of the time constant. The weakening of the relaxation peak indicates that the relaxation process of the grain boundary is impeded.

Considering that large differences existed between the bulk and grain boundary conduction ($f_b \gg f_{gb}$), we adopted the alternative representation Z'–Z''/f to process the impedance data of $CaMoO_4$,

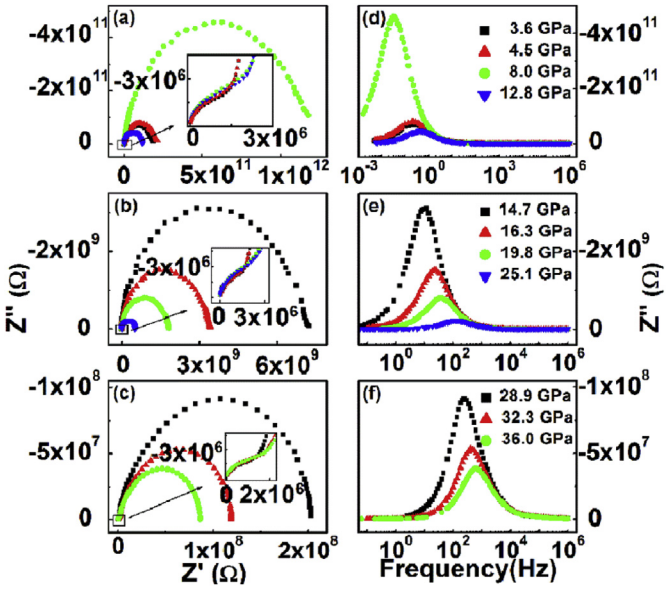

Fig. 1. (a)–(c) The impedance spectra Z''–Z' and (d)–(f) the frequency dependence of imaginary part of Z''–f plots of $CaMoO_4$ under compression. Inset: enlargement of impedance spectra in high frequency region.