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Electrical conductivity and thermal expansion behavior of $MMoO_4$ (M = Ca, Sr and Ba)

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ABSTRACT

Alkaline earth (Ca, Sr, Ba) molybdates were synthesized by solid state reaction route. The compounds were characterized by powder-XRD, TG–DTA techniques. The electrical conductivities of these compounds were measured by AC-impedance technique at 673–1073 K. The activation energies of electrical conduction of $CaMoO_4$, $SrMoO_4$ and $BaMoO_4$ were found to be 1.29 ± 0.01 eV, 1.33 ± 0.01 eV and 1.31 ± 0.01 eV respectively. The linear thermal expansion of these molybdates was measured by dilatometry. The mean coefficients (α_m) of thermal expansion for these compounds were found to be in the range of $9.38 \pm 0.18 \times 10^{-6}$–$12.96 \pm 0.25 \times 10^{-6}\ K^{-1}$ at 305–1005 K temperature range. The diffusion coefficient (D) values of oxide ion conduction for these molybdates were determined and found to be in the range of $9.48 \pm 0.02 \times 10^{-14}$–$3.32 \pm 0.01 \times 10^{-10}$ for $CaMoO_4$, $5.86 \pm 0.02 \times 10^{-14}$–$2.50 \pm 0.01 \times 10^{-10}$ for $SrMoO_4$ and $3.46 \pm 0.02 \times 10^{-14}$–$1.22 \pm 0.01 \times 10^{-10}\ cm^2\ s^{-1}$ for $BaMoO_4$ at 673–1073 K range of temperature.

1. Introduction

Molybdenum is a very important fission product in thermal and fast reactor fuels [1–3]. Around ~13% of the total fission products produced from U-235 fission are Mo (isotope) [1–3]. Molybdenum found in the form of molybdenum oxide in the irradiated fuel pin and forms various compounds of molybdates under suitable thermodynamic conditions [4]. Alkaline earth molybdates are the most common compounds found in the uranium oxide fuel fission as an interaction product of alkaline earth elements like Sr and Ba (fission product, Sr ~ 5%, Ba ~ 3.4%) with molybdenum oxide. The formation of $MMoO_4$, (M = Ca, Sr, Ba) compounds in the supercalcine-ceramics (a potential waste immobilization matrix) is also known [5–7]. These molybdates form ABO_4 type compounds, where A = Ca, Sr, Ba; B = Mo, W (Scheelite type structure), having tetragonal crystal structure [8,9]. Apart from its relevance to nuclear technology, scheelite type ABO_4 compounds are known to have interstitial oxide ions as the current carriers in their crystal structure [10–13] and can find applications in oxygen sensing devices. The thermodynamic properties of these compounds are well explored by various researchers [14]. The heat capacity values of $SrMoO_4$ and $BaMoO_4$ compounds were studied by Singh et al. [14]. But their thermal expansion and electrical properties are not well studied. In the present study, $CaMoO_4$, $SrMoO_4$ and $BaMoO_4$ compounds were synthesized by solid state reaction route and characterized by powder-XRD, TG–DTA. The electrical transport properties of these compositions were measured at 673–1073 K and were compared based on electropositive character of Ca, Sr and Ba cations in these compounds. The linear coefficient of thermal expansion of these alkaline earth molybdates was measured by dilatometry. The experimental results obtained on thermal expansion and electrical conductivity is discussed in this paper.

2. Experimental details

2.1. Synthesis and characterization of the powders of $CaMoO_4$, $SrMoO_4$ and $BaMoO_4$

The preparations of the alkaline earth metal (Ca, Sr and Ba) molybdates were done by solid state reaction route. The stoichiometric amounts of alkaline earth metal carbonates (MCO_3) were mixed with molybdenum oxide (MoO_3) in a mortar–pestle and ground thoroughly to get a homogeneous mixture. Then the mixture was pelletised and heated at 823 K for 3 h s in air ambience in a furnace. The product formed was characterized by powder-XRD for phase identification. Philips X'pert Pro MPD, θ–θ system with Cu Kα radiation monochromatized with curved graphite crystal placed infront of the NaI (Tl) scintillation detector was used in the step scan mode with a step size of 0.02° for 5 s counting time at each step. M/s. SETARAM-SETSYS-Evolution model was used for recording TG–DTA data at 298–1273 K in air ambient with a heating rate of 5 K/min and cooling rate of 10 K/min. The solid state reaction of the reactants leading to the product is shown in Eq. (1).

$$MCO_3 + MoO_3 \xrightarrow{823\ K/3\ h} MMoO_4 + CO_2 \uparrow \quad (1)$$

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(where, M = Ca, Sr and Ba).

The chemical composition of the phase pure compounds was analyzed by ICP-OES and AAS technique and is found to maintain M/Mo mole ratio: 1:1, where M = Ca, Sr, Ba.

2.2. Electrical conductivity measurements of $CaMoO_4$, $SrMoO_4$ and $BaMoO_4$ pellets

The electrical conductivity measurements on $CaMoO_4$, $SrMoO_4$ and $BaMoO_4$ were carried out by AC impedance technique. The pellets were prepared in a hydraulic pellet press (Ms. Kimaya Engineers, India) by using a tungsten carbide die and plunger and then the pellets were sintered at 1023–1273 K for 10 h s in air ambience. These sintered pellets (around 10 mm dia and 2–3 mm thickness) were used for electrical resistivity measurements. The bottom and top flat surfaces of the pellets were metalized using Ag-paste. The metalized pellets were contacted with Pt-disk shaped electrodes as shown in Fig. 1. The sample, electrodes and thermo-couple assembly is enclosed inside a one end closed alumina tube [15,16]. In this experiment, sample is sandwiched between the two electrodes and firm contact is ensured by tightening the alumina disks with stainless steel nut bolt on both side of the pellet as shown in Fig. 1. The Pt-wires spot welded to the platinum disks were used as leads to measure electrical resistance of the sample at various temperatures. The sample assembly was placed inside the cell and the cell was put inside the furnace well. The temperature of the furnace was controlled by a programmable PID temperature controller with ±1 K accuracy. The sample temperature was measured with a K-type (chromel–alumel) thermocouple placed at about 2 mm from the sample in the conductivity measurement cell. Resistances of the sample were measured at each 50 K interval. The impedance (Z) measurements were carried out using an Autolab Frequency Response Analyser (FRA) in the frequency range of 100 Hz–1 MHz. The resistance of the samples at various temperatures was determined by fitting the data of $-Z''$ ($Z_{imaginary}$) vs. Z' (Z_{real}) Nyquist plot using fit and simulate functions available in the Autolab FRA system. The real part of the semicircle ($-Z''$ vs. Z') is taken as the resistance of the sample at a particular temperature. The fitting of the semicircle was done by trial and error method on assuming various equivalent circuit models available with the software provided by Autolab. The equivalent circuit that fits all the points on the semicircle with minimum error is taken as the accepted model and the values of R and C calculated by the model for a particular temperature were taken as the accepted value. The conductivity of the samples was calculated using the formula given in the Eq. (2).

$$\sigma = (L/A) \times (1/R) \tag{2}$$

where L = the length of the pellet (cm), A = cross-sectional surface area of the cylindrical pellet (cm^2), R = resistance of the pellet, thereby we got σ in S cm^{-1}. The specific impedance of the samples is calculated by multiplying A/L ratio of the pellet with impedance values ($Z_{im} = Z''$ or $Z_{re} = Z'$) at all frequencies and at all temperatures then plotted as (Z_{im}/ohm cm) vs. (Z_{re}/ohm cm).

2.3. Thermal expansion measurements of $CaMoO_4$, $SrMoO_4$ and $BaMoO_4$ pellets

Thermal expansion measurements of $CaMoO_4$, $SrMoO_4$ and $BaMoO_4$ pellets of around 10 mm dia. and 10 mm height were carried out by dilatometry in the temperature range 298–800 K in air, by using a home-built apparatus [17,18]. Linear Variable Differential Transformer (LVDT) was used as the displacement sensor. The instrument was calibrated by measuring % thermal expansion of known standard single crystal of MgO [19] and ThO_2 pellets [20]. The experimentally measured value of MgO was interpolated at 2 deg. interval and plotted against temperature. The % thermal expansion was fitted to a polynomial equation of 3rd order. The % expansion obtained at various temperatures by using literature data and experimental data are compared within the measured temperature range. The difference in % thermal expansion reported in the literature (fitted value of equation reported in the literature) and experimentally measured for MgO is added to the experimentally measured value of ThO_2. The corrected value of ThO_2 is compared with the ThO_2 literature value by Belle and Berman [20]. The following equations (Eqs. (3)–(5)) are used to find out the corrected value of ThO_2 using MgO as the standard.

$$\text{MgO correction value} = \%\ \text{expansion of MgO using literature equation} - \%\ \text{expansion experimental value of MgO using interpolation} \tag{3}$$

$$\text{MgO corrected}\ \%\ \text{expansion of ThO}_2 = \text{Experimental}\ \%\ \text{expansion of ThO}_2 + \text{MgO correction value as given in Eq. (3)} \tag{4}$$

$$\text{The MgO corrected ThO}_2\text{value is compared with literature value given by Belle and Berman} \tag{5}$$

The literature value and corrected values of ThO_2 are found to be in good agreement. Same procedure is applied to cross check the % thermal expansion of MgO by adding difference of ThO_2 (fitted) and ThO_2 experimental and compared with MgO (literature value/fitted). In this study, the difference in fitted value and experimentally measured value of standard MgO single crystal is taken as the correction factor for the samples studied. The densities and dimensions of the pellets were once again measured after the thermal expansion measurements were complete. The dimensions were found to be unchanged. The percentage of average/mean linear thermal expansion is calculated using Eq. (6).

$$\%\ \text{TE} = (\Delta L/L) \times 100 \tag{6}$$

The coefficient of thermal expansion (average CTE = $\alpha_m = \alpha_{av}$) of the compounds was calculated by using the formula given in Eq. (7).

$$\text{Average or mean CTE} = \alpha_m = (\Delta L/L) \times (1/\Delta T) \tag{7}$$

where ΔL = change in length, L is the length of the pellet, ΔT = change in temperature in K.

3. Results and discussions

3.1. Phase identification by powder-XRD

The powder-XRD patterns (Fig. 2) of the compounds confirmed the formation of crystalline single phase alkaline earth metal molybdates ($CaMoO_4$, $SrMoO_4$ and $BaMoO_4$). There are no reactant phases detected in the XRD pattern of the samples. The XRD patterns of the compounds were indexed by using X-Pert' Pro software and found to stabilize in the tetragonal crystal system (Space Group: $I4_1/a$. (88) Scheelite type structure (ABO_4)). The lattice constants of these compounds were calculated and shown in Table 1. The values determined on indexing the XRD pattern were compared with the literature values [21] and found to agree well

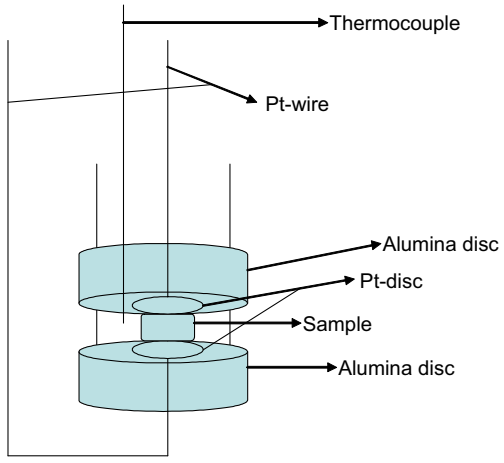

Fig. 1. Schematic of sample pellet and electrode assembly in the high temperature electrical conductivity cell.

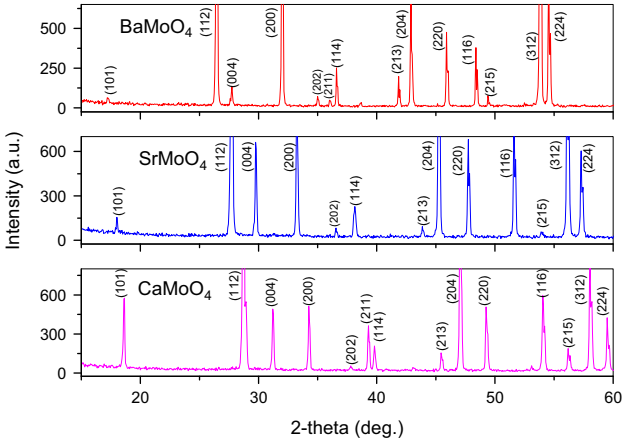

Fig. 2. XRD patterns of $CaMoO_4$, $SrMoO_4$ and $BaMoO_4$.