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Synthesis, structural and microwave dielectric properties of $Al_2W_{3-x}Mo_xO_{12}$ ($x = 0–3$) ceramics

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ABSTRACT

Low dielectric ceramics in the $Al_2W_{3-x}Mo_xO_{12}$ ($x = 0–3$) system have been prepared through solid state ceramic route. The phase purity of the ceramic compositions has been studied using powder X-ray diffraction (XRD) studies. The microstructure of the sintered ceramics was evaluated by Scanning Electron Microscopy (SEM). The crystal structure of the ceramic compositions as a result of Mo substitution has been studied using Laser Raman spectroscopy. The microwave dielectric properties of the ceramics were studied by Hakki and Coleman post resonator and cavity perturbation techniques. $Al_2Mo_xW_{3-x}O_{12}$ ($x = 0–3$) ceramics exhibited low dielectric constant and relatively high unloaded quality factor. The temperature coefficient of resonant frequency of the compositions is found to be in the range −41 to −72 ppm/°C.

1. Introduction

Past few decades have witnessed revolutionary changes in wireless communication, which was strongly accompanied by the development of microwave dielectric ceramics with improved properties. Circuit miniaturization and integration of multi components in single device are great challenges to surmount, as far as modern microelectronics scenario is concerned. Low temperature cofirable ceramics (LTCC) technology predominates all other existing techniques to meet this task. It provides high circuit density by the integration of different passive components to a 3-D wiring circuit board comprising of thin layers of low dielectric ceramics and conductors. The recent surge in wireless communication rigorously demand novel microwave dielectric ceramics with stringent properties such as low dielectric constant, low loss tangent, near zero temperature coefficient of resonant frequency and low sintering temperature. Most of the material systems having good microwave dielectric properties possess high sintering temperature, which limits their use in LTCC applications [1–3]. Low sintering temperature and chemical compatibility with metal electrodes are inalienable qualities required for LTCC materials. Though addition of low melting oxides or glass can reduce the sintering temperature, it is not preferred due to its adverse effect on the microwave dielectric properties. The successive attempts to reduce the sintering temperature of the ceramics lead to a new branch known as ultra-low temperature cofirable ceramics (ULTCC) which deals with ceramics having very low sintering temperatures [4,5]. The current interest in research is to develop materials in this category. Hence material researchers are focusing their efforts in developing new systems having ultra-low temperature cofirable materials.

Recent studies show that material systems containing TeO_2 and MoO_3 are most promising for LTCC applications [6–13]. Tellurium containing compounds usually show very low sintering temperature between 500 and 800 °C and good microwave dielectric properties [6–8]. Zhou et al. reported that $Bi_2Mo_2O_9$ ceramics sintered around 620 °C exhibits a dielectric constant of 38, Qxf value of about 12500 GHz and TCF value of +31 ppm/°C [9]. These authors also reported that Lyonsite type $Li_2(M^{2+})_2Mo_3O_{12}$ and $Li_3(M^{3+})Mo_3O_{12}$ (M = Zn,Ca,Al,In) materials have ultra low sintering temperature between 570 and 630 °C with dielectric constant between 9.5 and 11.1 [10].The Li_2O_3–Bi_2O_3–MoO_3 ternary system is another useful ceramic composition falling under this category [11]. Feteira and Derek studied the microwave dielectric properties of $Bi_2W_2O_9$ ceramics and their chemical compatibility with metal electrodes, a potential candidate material for LTCC applications [12]. Yoon et al. reported the microwave characterization of AWO_4 (A = Mg,Zn,Mn,Ca,Sr,Ba) ceramics having scheelite and wolframite structures and correlates the microwave dielectric properties with the ionic radii of A site cations and the crystal structure [13].

It is clear from the existing reports that tungstate and molybdate systems are versatile materials for LTCC applications. However, only a few literature are available on the structure-property relationship of this important class of material systems. Metal

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tungstates and molybdates belong to $A_2M_3O_{12}$ family are well known for their negative thermal expansion coefficient and trivalent ionic conductivity [14–17]. Apart from these, they have potential applications as electrolytes in solid state ionic devices, fuel cells, host material in lasers, etc. [18,19]. High chemical flexibility of this family allows the substitution of A site by trivalent transition metal ions or rare earth ions and thereby helps to tune the properties as per user requirement. In view of the above, we have carried out a systematic study on the preparation and structure-property relation of $Al_2W_{3-x}Mo_xO_{12}$ (x = 0–3) ceramic system.

2. Experimental procedure

The $Al_2W_{3-x}Mo_xO_{12}$ (x = 0–3) samples were prepared by solid state ceramic route. Al_2O_3 (INDAL MR 06, India), MoO_3 (MERCK, India), WO_3 (HIMEDIA, India) were used as the starting materials. The stoichiometric proportions of the raw materials were accurately weighed and mixed using an agate mortar with double distilled water as the mixing medium. The slurry obtained was dried inside a hot air oven and the resultant mixture was calcined at 700 °C for 1 h except $Al_2W_3O_{12}$ which was calcined at 900 °C for 2 h. The calcined powders were mixed with 5 wt% poly vinyl alcohol (PVA) as binder and shaped in to cylindrical compacts using a tungsten carbide die at 250 MPa pressure in a hydraulic hand press. The pellets were sintered in a programmable furnace at a temperature 1060 °C for 2 h in the case of $Al_2W_3O_{12}$ and 810 °C for 2 h for rest of the compositions. The crystal structure and phase purity of the sample were studied using powder X-ray diffraction (XRD) technique (M/S Brucker AXS, Germany). The sintered samples were thermally etched and surface morphology was studied using scanning electron microscope (JEOL model JSM-6390 LV, Tokyo, Japan). The microwave dielectric properties were measured using a Vector Network Analyzer (Agilent E8362B, USA). The dielectric constant and quality factor of the samples were measured by Hakki and Coleman post resonator technique and resonant cavity method respectively [20,21]. The temperature coefficient of resonant frequency 'τ_f' was also measured in the temperature range 30–100 °C. The Raman spectra of the ceramic compositions under study were recorded using a Bruker RFS 1001s spectrophotometer with a Nd:YAG laser of wavelength 1064 nm using Ge target.

3. Results and discussion

The samples under study are hereafter referred as AlW ($Al_2W_3O_{12}$), $AlMW_2$ ($Al_2MoW_2O_{12}$), AlM_2W ($Al_2Mo_2WO_{12}$), and AlM ($Al_2Mo_3O_{12}$) respectively. The phase purity of the samples is studied by powder X-ray diffraction. Fig. 1 shows the room temperature X-ray diffraction patterns of the sintered and powdered samples. The XRD data indicates that both the parent and substituted phases are single phase in nature. The X-ray diffraction pattern of AlW is indexed with standard JCPDS (28-36) pattern having orthorhombic structure (space group pbcn) and is matching well with the standard pattern. The observed unit cell parameters of AlW are calculated as a = 9.1394 Å, b = 12.570 Å and c = 9.033 Å. The XRD patterns of the remaining samples with x = 1–3 are also shown in Fig. 1. The systematic substitution of W by Mo results in slight peak shifting and intensity variation in the XRD patterns. Fig. 2 shows a closer view of the XRD patterns of AlW and AlM at 2θ range between 20 and 30°. It is clear from the figure that all the peaks of AlM are shifted slightly on the higher 2θ side. In the XRD pattern of AlW, (0 3 1) peak is clearly visible as a single peak where as in the XRD pattern of AlM the peaks appeared at (1 1 2) and (2 1 1) are intercalated with the (0 3 1) peak and appeared as a shoulder. Although $Al_2Mo_3O_{12}$ composition is reported as orthorhombic as per JCPDS (23-764), the time of flight neutron diffraction studies show that this material exists in monoclinic structure having eight formula units per unit cell with $P2_1/a$ space group [22].

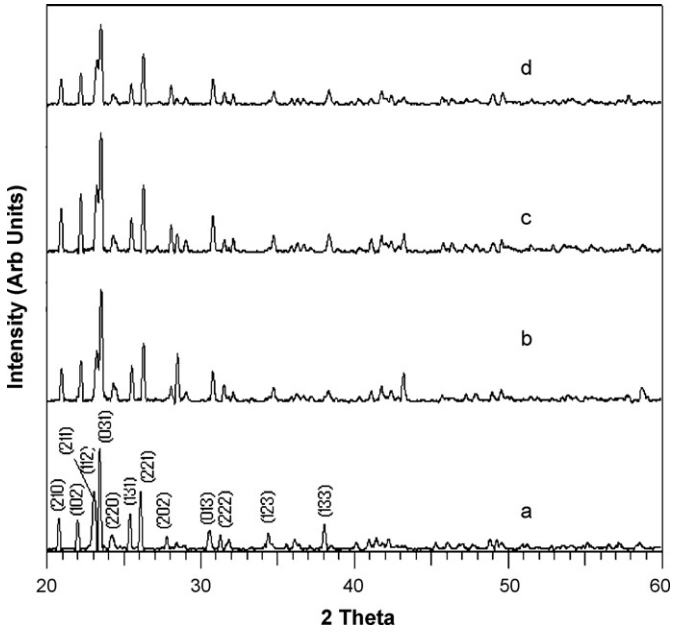

Fig. 1. X-ray diffraction patterns of $Al_2W_{3-x}Mo_xO_{12}$ ceramics (a) AlW (b) $AlMW_2$ (c) AlM_2W and (d) AlM.

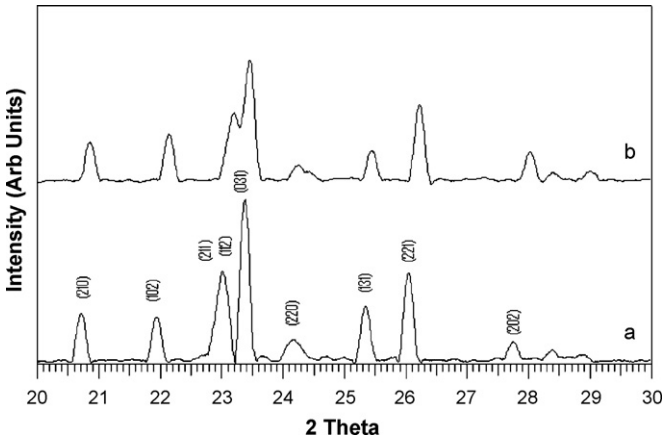

Fig. 2. X-ray diffraction patterns of AlW and AlM in the 20–30° 2θ region.

Fig. 3 shows the typical Scanning Electron Microscopy (SEM) images of AlW_2M and $AlWM_2$ ceramics. Both the samples exhibit dense microstructure with closely packed polygonal and rectangular grains having size ranging from 2 to 6 μm. However, the average grain size for $AlWM_2$ is relatively less compared to that of AlW_2M.

The density and microwave dielectric properties such as dielectric constant, quality factor and temperature coefficient of resonant frequency of the ceramic compositions under study are compiled in Table 1. Aluminum tungstate (AlW) exhibits a dielectric constant of 6.3 at microwave frequency. From Table 1, it is clear that the substitution of Mo in place of W reduces the bulk density of the sintered ceramic samples. However, no significant variation in dielectric constant is noticed with respect to an increase in Mo concentration. A sharp decrease in sintering temperature is also found for the molybdenum rich samples due to the low melting point of MoO_3.

Fig. 4 shows the variation of unloaded quality factor and dielectric constant with respect to Mo concentration. An interesting point to be noted is the improvement of the quality factor of the material with increase in Mo concentration. This improvement in quality factor can be attributed to the ordering of the tetrahedral networks as a result of Mo substitution.

The temperature coefficient of resonant frequency, τ_f, of the sintered samples are measured and plotted in Fig. 5. It shows a decreasing trend as molybdenum is substituted for tungsten except for $AlMW_2$. All the samples under study exhibit a low τ_f value in the range −41 to −72 ppm/°C, although the Mo rich samples exhibit relatively low τ_f compared to others.

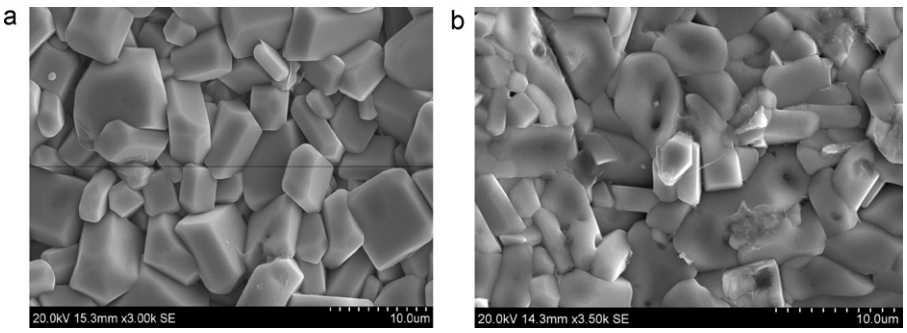

Fig. 3. SEM micrographs of (a) AlW_2M and (b) $AlWM_2$ ceramics.

Table 1
Sintering temperature, density and microwave dielectric properties of $Al_2W_{3-x}Mo_xO_{12}$ ceramics.

Composition	Density (g/cc)	Dielectric constant (ε_r)	Resonant frequency (GHz)	Unloaded quality factor (Qu)	Temperature coefficient of resonant frequency (τ_f) (ppm/°C)
AlW	4.75	6.3	12.8365	810	−67
$AlMW_2$	3.91	5.8	13.859	2451	−72
AlM_2W	3.35	6.3	11.770	3104	−55
AlM	2.98	6.4	11.977	4110	−41

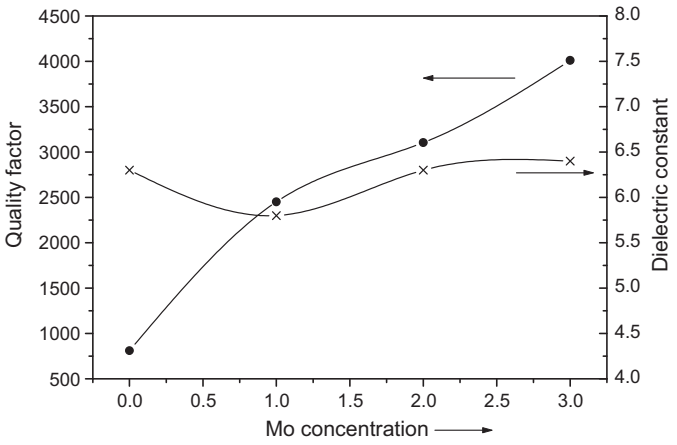

Fig. 4. Variation of dielectric constant and quality factor with respect to Mo concentration.

Since the X-ray diffraction studies did not provide any clear evidence for the structural change with respect to Mo substitution, Laser Raman studies have been carried out to obtain better understanding about the structure-property relationship of these compositions. The internal vibrational modes of the free MoO_4^{2-}/WO_4^{2-} tetrahedra with Td symmetry are classified as ν_1 (symmetric stretching mode), ν_2 (symmetric bending mode), ν_3 (asymmetric stretching mode), and ν_4 (asymmetric bending mode) and all the four vibrations are Raman active [23]. In the Raman spectrum of AlW, the symmetric stretching vibrations of WO_4^{2-} tetrahedra are observed as a strong band at 1048 cm^{-1} and a small feature at 992 cm^{-1} (Fig. 6). It is reported that the WO_4^{2-} tetrahedra in $Al_2W_3O_{12}$ are more regular in shape [24]. This could be the reason for the less number of peaks observed in the symmetric stretching vibration region though two crystallographically distinct WO_4^{2-} tetrahedra (occupying at C1 and C2 sites) exist in this compound. When one W is replaced with Mo, the strongest symmetric stretching vibration remains at more or less same wavenumber region although the intensity of the mode at 991 cm^{-1} is slightly increased. As the Mo concentration increases, the vibrational mode near 996 cm^{-1} become more intense than that at 1048 cm^{-1}. In addition, the numbers of asymmetric stretching vibrations also become

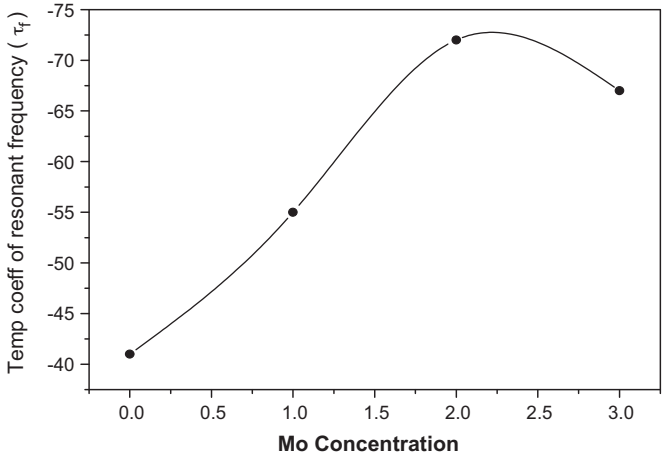

Fig. 5. Variation of τ_f with respect to Mo concentration.

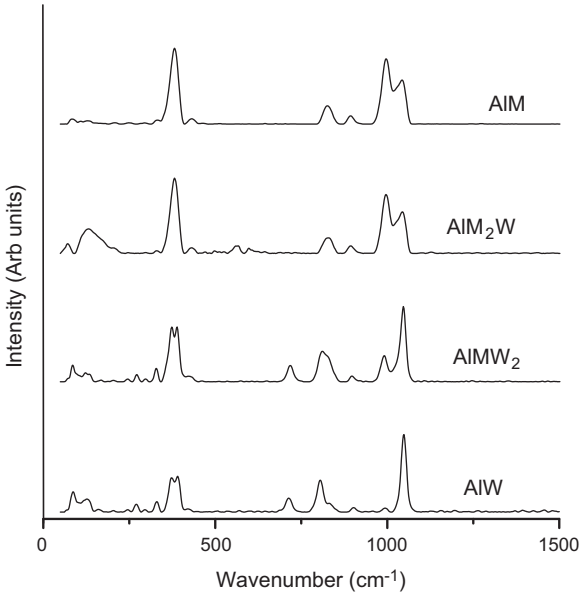

Fig. 6. Raman spectra of $Al_2W_{3-x}Mo_xO_{12}$ ceramics.

less compared to W-rich compositions. Another interesting feature worth mentioning in the Raman spectra of Mo rich compositions is the relatively intense symmetric bending vibrations of MoO_4^{2-} tetrahedra compared to that of stretching vibrations. The modes observed below 300 cm^{-1} corresponds to the translational and rotational modes of W/MO_4^{2-} tetrahedra, metal–oxygen stretching modes, etc. An unambiguous assignment of these modes is not possible. The systematic variations observed in the Raman spectra of $Al_2W_{3-x}Mo_xO_{12}$ compositions show that single phase microwave ceramic materials can be formed by progressive replacement of W by Mo.

The obtained Raman spectrum of $Al_2W_3O_{12}$ in the present study is comparable with earlier reports [25]. Maczka et al. reported the high pressure Raman study of $Al_2W_3O_{12}$ wherein this compound exhibits a phase transition from orthorhombic (D_{2h}^{14}) to monoclinic (C_{2h}^{5}) phase. The monoclinic phase of $Al_2W_3O_{12}$ exhibits two strong vibrational modes in the symmetric stretching region instead one strong Raman mode ~1050 cm^{-1} for the orthorhombic phase. Interestingly, the Raman spectrum of $Al_2Mo_3O_{12}$ exhibits the same vibrational features similar to that of $Al_2W_3O_{12}$ under pressure which has monoclinic structure [26]. Further, Forzatti et al. also reported the Raman spectra of monoclinic $Al_2Mo_3O_{12}$and $Cr_2Mo_3O_{12}$, with same internal vibrational features as reported in the present study [27]. It is also reported that the monoclinic and orthorhombic modifications of $A_2Mo_3O_{12}$ are strictly related to each other and further more that the monoclinic to orthorhombic transformation in these materials is expected to result from minor cooperative rotations of the polyhedra around axes passing through their corners. Hence it can inferred that a structural phase transition occurs while W is completely replaced by Mo in $Al_2W_{3-x}Mo_xO_{12}$.

4. Conclusion

$Al_2W_{3-x}Mo_xO_{12}$ (x = 0–3) ceramics have been prepared through solid state ceramic route. Structure and microstructure of the compositions have been studied using powder X-ray diffraction, Laser Raman spectra and Scanning Electron Microscopy. X-ray diffraction studies show that the compositions under study are single phase in nature. Dense and pore free microstructure is observed for the sintered ceramics. Microwave dielectric properties of the sintered ceramic compacts show low dielectric constant in the range 5.8–6.4, unloaded quality factor in the range 810–4110, and temperature coefficient of resonant frequency in between −41 and −72 ppm/°C. Laser Raman studies show that $Al_2W_3O_{12}$ has orthorhombic structure whereas $Al_2Mo_3O_{12}$ has monoclinic structure.

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