Structural and electrical properties of Li$_2$Pb$_2$Sm$_2$W$_2$Ti$_4$Ta$_4$O$_{30}$ ceramics

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ABSTRACT

The polycrystalline sample of complex tungsten-bronze compound Li$_2$Pb$_2$Sm$_2$W$_2$Ti$_4$Ta$_4$O$_{30}$ was prepared by a high-temperature solid-state reaction technique. Room temperature X-ray diffraction (XRD) study suggests the formation of a single-phase compound. Microstructure of the pellet sample was studied by scanning electron microscope. The temperature variation of dielectric constant shows dielectric anomaly in the sample. Study of electrical properties (impedance, conductivity, etc.,) of the material exhibits a strong correlation between its micro-structure (i.e., bulk, grain boundary, etc) and electrical parameters. A typical Arrhenius behavior was observed in the temperature dependence of dc conductivity. Copyright © 2014 VBRI press.

Keywords: Ceramics; X-ray diffraction; microstructure; ferroelectricity; impedance spectroscopy.

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Introduction

The discovery of interesting non-linear dielectric property in BaTiO$_3$ attracted attention of researchers to study ferroelectric properties of a large number of compounds of similar and/ or different structural family useful for device applications [**1, 2**]. Among all the ferroelectric oxides known today, tungsten bronze (TB) structural families are found to be important for pyroelectric and ferroelectric devices above room temperature. The tungsten bronze (TB) structure of a general formula [(A$_1$)$_2$(A$_2$)$_4$](C)$_4$[(B$_1$)$_2$(B$_2$)$_8$]O$_{30}$ (where A-sites are occupied by mono to tri-valent cations, B-sites are occupied by tetra-hexavalent ions and C-site either unfilled or occupied by small ions), are complex and disordered, they have also been found much more useful for many devices. The properties of this type of materials can be tailored by making suitable modifications at A, B or/and C sites. In

view of the above, some TB structured ferroelectrics have been found special in the family of oxide-materials for device applications. Because of the importance of the TB structured materials, a large number of compounds of this family have been studied in the past in the form of single crystal, thin film or/and ceramic form. Structural, ferroelectric and electrical transport properties of some compounds (related to this paper) such as $Pb_3R_3Ti_5Nb_5O_{30}$ (R = rare earth ion) have been studied by several workers [3-8]. Attempts have also been made to develop some ferroelectrics with multi-valence complex TB structure [9-11] to enhance some of their properties. It is now known that many complex or disordered compounds provide interesting properties. Detailed literature survey shows that not much work have been done on the compounds having all six valence ions. However, structural and dielectric properties of $Na_2Pb_2La_2W_2Ti_4Nb_4O_{30}$, ferroelectric properties in $Na_2Pb_2Pr_2W_2Ti_4Ta_4O_{30}$, dielectric and electrical properties of $Na_2Pb_2La_2W_2Ti_4Ta_4O_{30}$, ferroelectric and related properties of $Li_2Pb_2Pr_2W_2Ti_4Nb_4O_{30}$ [12-15] have been reported by our co-worker previously. As the dielectric and related properties in the $Li_2Pb_2Sm_2W_2Ti_4Ta_4O_{30}$ (LPSWTT) complex system is not known, we have synthesized and studied various properties of the material.

Experimental

The polycrystalline sample of $Li_2Pb_2Sm_2W_2Ti_4Ta_4O_{30}$ (LPSWTT) was synthesized by a solid-state reaction technique using high-purity (AR grade) ingredients: Li_2CO_3, TiO_2, Ta_2O_5 and WO_3 (99%, M/s LOBA Chemie Pvt. Ltd. India), PbO (99.9% M/s E Merk India Ltd), Sm_2O_3 (99.9%, M/s Indian rare earth Ltd). These oxides and carbonate were mixed in dry (air) and wet (methanol) medium for several hours in agate mortar. The mixed material was calcined at an optimized temperature (1100^0C) on the basis of repeated firing and mixing for 6 h in alumina crucible. X-ray diffraction (XRD) pattern on calcined powder was recorded at room temperature using X-ray powder diffractometer (Rigaku). The CuK$_\alpha$ radiation (λ=1.5405A^0) was used to collect data in a wide range of Bragg's angle (θ) ($20^0 \leq 2\theta \leq 80^0$) at a scanning rate of 3 deg/min for preliminary structural analysis. Using PVA (binder) mixed calcined powder the cylindrical pellet samples (diameter 10 mm and 1-2 mm thickness) were fabricated under a uni-axial pressure of 4×10^6 Nm^{-2} (with a hydraulic press). All the pellets were then sintered at 1150^0C in air atmosphere for 4 h to get mechanically stable, strong and high density samples. The polished sintered pellets were electroded with high purity and quality silver paste and, dried at 160^0C for 8 hrs before taking dielectric and electrical measurements. The surface morphology of a gold-coated pellet sample was recorded by JEOL JSM-5800 scanning electron microscope (SEM). The capacitance, dissipative factor, and impedance parameters on silvered-coated pellet were obtained as a function of temperature (25-500^0C) in a wide range of frequency (1 kHz-1MHz) using a computer-controlled phase sensitive impedance/LCR meter (PSM-4NL Model: 1735, UK) with a laboratory-designed and fabricated sample holder and

furnace. To record the temperature at small interval, a chromel-alumel thermo-couple and KUSAM MECO 108 digital milli-voltmeter was used.
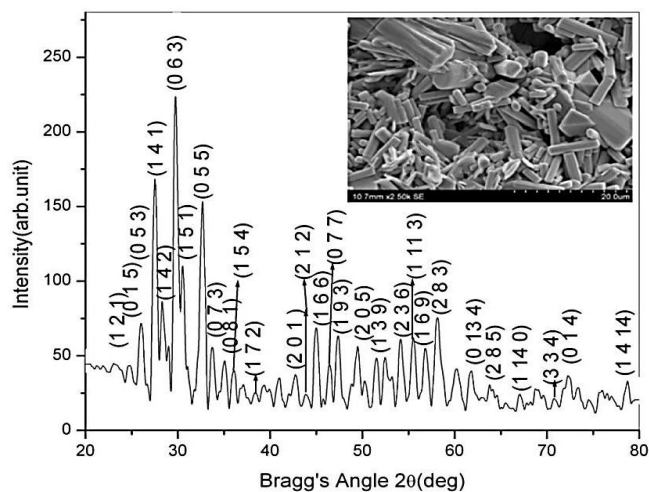
Fig. 1. X-ray diffraction pattern of LPSWTT at room temperature SEM micrograph of LPSWTT (inset).

Results and discussion

Structural study

The X-ray diffraction (XRD) pattern of $Li_2Pb_2Sm_2W_2Ti_4Ta_4O_{30}$, recorded at room temperature on its powder sample, is shown in **Fig. 1** The XRD pattern consists of large number sharp and single peaks, which are different from those of the ingredients confirms the formation of new compound [16] in a single phase. Since TB structure is generally crystallized in tetragonal or orthorhombic structure, most of the peaks of XRD pattern were indexed in these two systems with different unit cell configurations using a standard computer program package "POWD" [17]. A good agreement between observed (obs.) and calculated (cal.) inter planar spacing of each reflection were found to be in a particular unit cell configuration of orthorhombic crystal system. The selected lattice parameters (a, b and c) of a unit cell were refined using a least-squares refinement sub-routine of POWD. The refined lattice parameters of the material are found to be consistent with those of some reported compounds of TB structure family [11]. Further, the crystallite or particle size (P) of the compound was calculated using the broadening of some widely spread (over Bragg angles) strong and medium reflections in the Scherrer's equation: $P_{hkl} = \frac{K\lambda}{\beta_{1/2} Cos\theta_{hkl}}$ [18], where k (constant) = 0.89, λ=1.5405^{0}A and $\beta_{1/2}$= full width at half maximum (in radians). The average value of P_{hkl} is found to be 11nm. The least-squares refined unit cell parameters are: a=4.2600(2) Å, b=20.6582(2) Å, c=18.2898 (2) Å (the numbers indicated in parenthesis are estimated standard deviation in unit cell parameters). As the TB structure is built on five crystallographic sites, it is difficult to precisely determine the Sm^{+3} ions coordination (12- or 15- fold coordination) based on the current results. However, the numerous structural studies show that the rare -earth ions predominantly prefer the A$_1$ tunnels [8].

The SEM micrograph of the compound at room temperature is shown in **Fig. 1** (in set). The texture and nature of micrograph confirmed the polycrystalline nature of the material. It was observed that the rod like grains of size in the range 2–12 μm are homogenously distributed over the entire surface of the sample with inter-grain porosity.
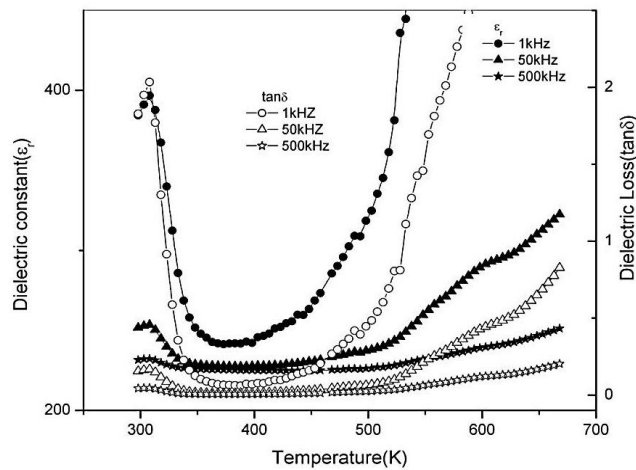

Fig. 2. Variation of dielectric constant (ε$_r$) and loss tangent (tanδ) of LPSWTT as a function of temperature at 1, 50 and 500 kHz.
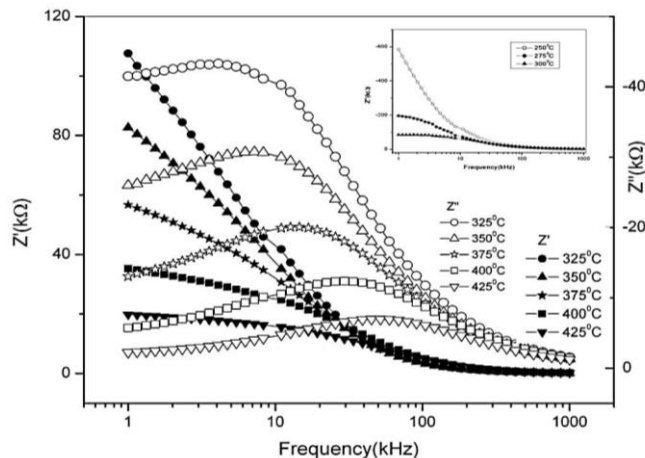
Fig. 3. Variation of Z' and Z'' with frequency of LPSWTT at selected temperatures.

Dielectric study

The temperature variation of relative dielectric constant (ε$_r$) and tangent loss (tanδ) at different frequencies (1 kHz, 50 kHz and 500 kHz) are shown in **Fig. 2**. The value of ε$_r$ increases on increasing temperature up to a temperature (referred as transition temperature (T$_c$)), and then decreases. The variation of tanδ with temperature follows the similar pattern as of ε$_r$. The transition temperature, room temperature dielectric constant and tangent loss of the material are found to be 35°C, 225 and 0.051 respectively. It is observed that the values of ε$_{max}$ (dielectric constant at T$_c$) at 1, 50, and 500 kHz is found to be 396, 253 and 232 respectively. The values of tanδ$_{max}$ (tangent loss at T$_c$) at same frequency are found to be 2.03, 0.18 and 0.04

respectively. The rate of increase of tanδ for the sample is slow/small in low temperature region, but at higher temperatures this rate increases significantly. The sharp increase in tanδ at higher temperatures may be due to scattering of thermally activated charge carriers and some defects in the sample [15]. At higher temperatures the conductivity begins to dominate, which in turn, is responsible for rise in tanδ. Also, at higher temperatures the contributions of ferroelectric domain walls to tanδ is less, which causes the rise in value of tan δ [15]. The value of ε$_{max}$ and tanδ$_{max}$of the titled compound decreases with rise in frequency. Such characteristic is normally found in a normal ferroelectric material. Additionally, a dispersion in tanδ on the higher temperature side can be seen **Fig.2** which is associated to ionic conductivity of the material, which may be related to loss of oxygen or PbO during sintering at high temperature.

Complex impedance analysis

Complex impedance spectrum is a novel and effective technique to study the electrical response of dielectric or ionic materials. The frequency dependence of electrical properties of a material is often represented in terms of complex impedance (Z) and electric modulus (M). The following the basic formalism or equations of impedance and electrical modulus which are normally used in this technique. They are related to each other as follows; complex impedance, $Z(\omega) = Z' - jZ'' = R_s - \frac{j}{\omega C_s}$, complex modulus, $M(\omega) = \frac{1}{\varepsilon(\omega)} = M' + j M'' = j \omega C o Z$, complex admittance $Y^* = Y' + jY'' = j\omega C_o \varepsilon^* = (R_P)^{-1} + j\omega C_p$ and complex permittivity $\varepsilon^* = \varepsilon' - j\varepsilon''$, where $\omega = 2\pi f$ is the angular frequency; C_0 is the geometrical capacitance, $j = \sqrt{-1}$. The subscripts p and s refer to the equivalent parallel and series circuit components respectively.

Fig. 3 shows the variation of Z' and Z'' as a function of frequency at some selected temperatures. It is observed that the value of Z' decreases with rise in frequency and temperature which indicates that the conduction is increasing with rise in frequency and temperature. At high frequency the value of Z' of each temperature coincides implying the possible release of space charge [19].

Like Z', the value of Z'' decreases on increasing frequency at all temperatures up to 300^{0}C. The non-existence of Z'' peak in this temperature region is due to the absence of current dissipation in the material.

For temperatures above 300^{0}C Z'' increases, attains a maximum value (Z''$_{max}$) and then decreases. The magnitude of Z''$_{max}$ decreases with temperature indicating an increasing loss in the resistive property of the sample. The value of Z''$_{max}$ shifts to higher frequencies with increasing temperature. This indicates the occurrence of relaxation in the system [15]. Peak broadening with increase in temperature suggests the presence of temperature dependent electrical relaxation phenomenon in the material. The relaxation process is due to the presence of immobile species at low temperatures and defects/vacancies at higher temperatures [20, 21].

Fig. 4 shows the temperature dependence of complex impedance spectra (Nyquist plot) of LPSWTT over a wide range of frequency (1000 Hz – 1MHz). The impendance is characterized by the appearance of semicircular arcs which is temperature dependent. At lower temperatures (up to 300^0C) complex impedance plots show single semicircular arc. At higher temperatures ($325 – 425^oC$) two semicircular arcs (with centre below the real axis) are observed. Most acceptable approach to interpret the depression of semicircles is statistical distribution of relaxation time [15]. The nature of plots at high temperatures suggests that the electrical response is composed of at least two semicircles; first due to bulk (grain) property of material whereas the second one (at high temperature) is due to presence of grain boundary [15] in the sample.
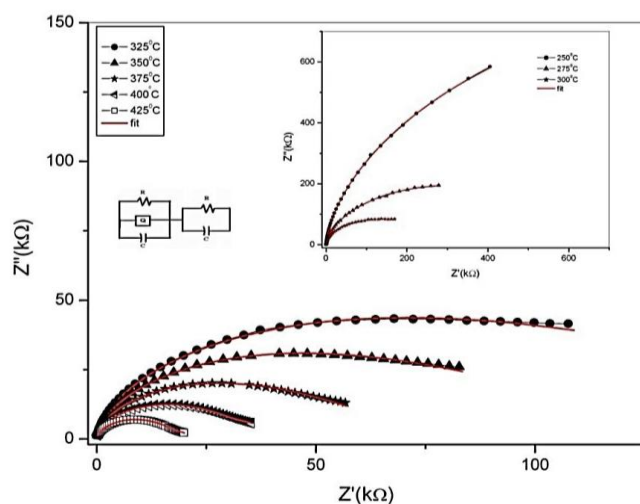

Fig. 4. Variation of Z″ with Z′ at different temperatures of LPSWTT.

Fig. 4 also compares the experimental complex impedance plots with a model fitted data using commercially available software ZSIMP WIN version 2.0. In an ideal case (Debye - like response) an equivalent circuit consists of parallel combination of (CQR) and (CR) where Q is known as constant phase element (CPE). The admittance of CPE is defined as Y (CPE) $=A_0$ (jω)^n $=A\omega^n+jB\omega^n$ with A= A_o Cos (nπ/2) and B= A_o Sin (nπ/2) where A_0 and n are frequency independent but temperature dependent parameters. A_0 determines the magnitude of the dispersion, and 0$\leq$ n $\leq$1 (for an ideal capacitor n=1, and for ideal resistor n = 0) [22].

A perfect semi-circle with its center at Z$^{'}$ axis is observed for an ideal Debye-type relaxation. But in the studied material we did not get Debye-type of relaxation. Thus, depressed semi-circles indicate the presence of non–Debye type of relaxation. It also manifests that there is a distribution of relaxation time instead of a single relaxation time in the material [15, 23]. The intercept of each semi-circle on real Z′ axis gives the contributions of bulk and grain boundary in the resistance/impedance. The semi-circles of the impedance spectrum have a characteristic peak occurring at a unique relaxation frequency usually referred as relaxation frequency (f_r) ($\omega_r = 2\pi f_r$). It can be expressed as ω_r RC = $\omega_r\tau = 1$, and thus f_r = 1/ 2πRC, where

τ is the relaxation time. The relaxation time due to bulk effect (τ_b) has been calculated using the equation $\omega_r\tau_b = 1$. Fig. 5 (inset) shows the variation of lnτ_b with inverse of absolute temperature (10^3/ T). The value of τ_b decreases with rise in temperature, and thus temperature dependent relaxation time for bulk follows the Arrhenius relation: τ_b = τ_o exp(-E_a / K_BT) where τ_o is the pre-exponential factor, K_B is Boltzmann constant and T is the absolute temperature. The calculated value of activation energy (E_a) is 0.96 eV which is consistent with the reported ones [15].
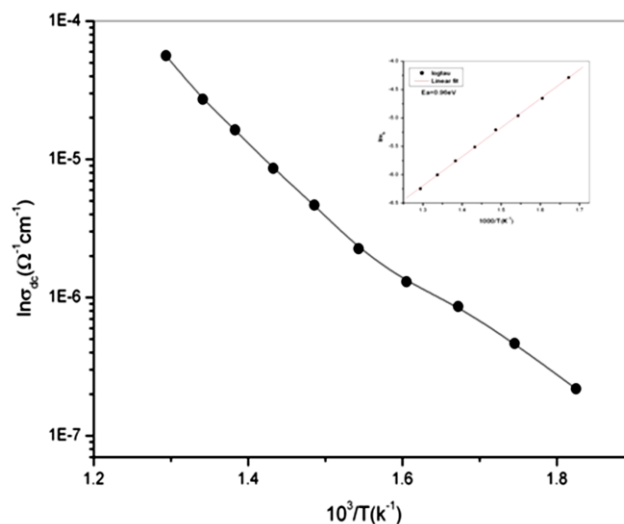
Fig. 5. Variation of dc conductivity with inverse of temperature of LPSWTT, variation of relaxation time (τ) as a function of reciprocal of temperature of LPSWTT (inset).

DC conductivity

Fig. 5 shows the variation of dc conductivity with respect to inverse of absolute temperature. The value of bulk conductivity of the material was evaluated from the complex impedance plots of the sample at different temperatures using the relation: σ_{dc} = t / R_bA, where R_b is the bulk resistance, t the thickness and A is the surface area of the sample respectively. The dc conductivity increases with rise in temperature confirming the negative temperature co-efficient of resistance (NTCR) behavior.

This plot follows the Arrhenius relation: $\sigma_{dc} = \sigma_o\, e^{-\frac{E_a}{K_BT}}$. The activation energy value estimated from the conductivity variation pattern was found to be 0.94eV which is almost same as that obtained from the relaxation time versus temperature curve.

Conclusion

Polycrystalline sample of a new ferroelectric compound, $Li_2Pb_2Sm_2W_2Ti_4Ta_4O_{30}$, was prepared by a high-temperature solid-state reaction technique. Room temperature X-ray analysis reveals the orthorhombic crystal structure in the studied compound. The SEM micrograph shows that the grains are homogenously distributed over the surface of the sample. Dielectric study shows the dielectric anomaly occurs at 308K which is just above the room temperature. Complex impedance analysis

of the compound shows that the material shows conduction due to bulk and grain boundary effect, NTCR-type behavior. The activation energy of the sample, estimated from the conductivity pattern and relaxation time is almost same indicates that the same type of charge carriers is responsible for both the conduction and relaxation phenomena.

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