ELECTRICAL TRANSPORT PROPERTIES STUDY OF A TUNGSTEN BRONZE-TYPE VANADATE CERAMIC BY IMPEDANCE SPECTROSCOPY AND ELECTRIC MODULUS

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Abstract- A ferroelectric ceramic oxide with tungsten bronze- type, $Li_2Pb_2Eu_2W_2Ti_4V_4O_{30}$, was synthesized by a conventional solid-state sinteringmethod.(DTA and TGA) technique optimized the preparation conditions of the material.X-ray diffraction (XRD) studyconfirms the formation of a single phasecompound with orthorhombic crystal structure. Scanning electron micrograph shows the polycrystalline nature of the material with uniform grain distribution throughout the sample.Dielectric studyshows the existence of two phase transition in the compound. Complex impedance spectroscopy techniques investigates it's microstructure and electrical properties as a function of frequency and temperature. Impedance studies indicate the existence of temperature dependent relaxation process in the material with multiple no of relaxation time. The variation of dc conductivity with temperature follows the Arrhenius behavior, and reveals the negative temperature coefficient of resistance (NTCR) nature of the material like a semiconductor. The frequency dependence of ac conductivity (fitting) at various temperature obeys the Jonscher's universal power law.

Keywords - A. Ceramics, B. X-ray diffraction, C. Microstructure. D. Ferroelectricity, E. Impedance Spectroscopy

I. INTRODUCTION

Tungsten bronze ceramic oxides are the popularly studied ferroelectrics next to perovskites. This wide family offers the possibility to tune the material response by changing the composition and useful for many devices such as ferroelectric random access memory, multi-layered capacitors, transducers, pyroelectric detectors, actuators [1–5]. The complex and disordered TB structure consists an arrays of distorted BO₆ octahedral sharing corners in such a way that three different types of interstices (A–C) are available for various cations substitution in the general formula $[(A_1)_2(A_2)_4(C)_4][(B_1)_2(B_2)_8]O_{30}$ or $[(A_1)_2 (A_2)_2(A_3)_2(C)_4][(B_1)_2(B_2)_4(B_3)_4]O_{30}$ along the 4-fold symmetry [6]. The A site again subdivided into twotypes (A_1, A_2) can be filled by largemonovalent, divalent, or trivalent ions. Two different Bsites (B_1, B_2) are filled by cations like Nb⁵⁺, Ta⁵⁺, V⁵⁺, W⁶⁺, Ti⁴⁺, and C site is small, generally remains empty occupied by Li, Er, etc.[7–9]. Hence tungsten bronze structure has a general formula $[(A_1)_2(A_2)_4(C)_4][(B_1)_2(B_2)_8]O_{30}$. Extensive literature survey on vanadium based TB compounds reveals that a good no.of work has already been reported with different chemical composition due to excellent industrial applications based on their ferroelectric, piezoelectric and non-linear optical properties[10-14]. Attempts have also been made to develop some ferroelectric vanadates with multi-valence complex TB compounds havingmono-trivalent ions substituted at the A site, and tetra-hexa valent ions substituted at the B site [15-18]. Though a large no of reports are found in open literature onTB structured vanadates, no work has been reported so far on temperature and frequency dependent dielectric and electrical properties of $Li_2Pb_2Eu_2W_2Ti_4V_4O_{30}$ using impedance spectroscopy . So we haveprepared the above complex tungsten bronze-structure compound with all the six valence elements (I-VI), and systematically studied its structural, dielectric and electrical properties at different frequency and temperature.

2. Experimental

The polycrystalline compound of $Li_2Pb_2Eu_2W_2Ti_4V_4O_{30}$ (LPEWTV) was prepared by a mixedoxide method using high-purity (AR grade) raw materials: Li_2CO_3 , PbO, Eu_2O_3 , TiO₂, V_2O_5 and WO₃ (all from M/s Loba Chemical Co. India). Theseoxides and carbonate were homogeneously mixed bygrinding the raw materials in dry (air) and wet(methanol) medium for 2 h in agate mortar. Thecalcination temperature was initially decided andlater optimized at 725⁰C using thermal analysis andrepeated firing and mixing for 4 h in an aluminacrucible. X-ray diffraction (XRD) pattern of calcinedpowder was recorded at room temperature usingX-ray powder diffractometer (Rigaku, Miniflex) with Cuk_{α} radiation ($\lambda = 1.5405$ Å) in a wide range of Bragg angles ($20^0 \le 2\theta \le 80^0$) at a scanning rate of 3 deg/min.

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 750^oC in air atmosphere for 4 h to get mechanically stable, strong and high density samples. The polished sintered pellet was electroded with high purity and quality silver paste and, dried at 150° C for 4 h before taking electrical measurements. The surface morphology of a gold-coated pellet sample was recorded by JEOL JSM-5800 scanning electron microscope (SEM). The dielectric parameters and electrical conductivity data of a sintered pellet were recorded using a computer-control Hioki 3532 LCR Hi-TESTER (Model: 3532, Japan) (with a laboratory-made sample holder and furnace in the temperature range of 25-500°C as a function of frequency (100 Hz to 1 MHz). A chromel-alumel thermo-couple and AGRONIC-161 digital milli-voltmeter were used to measure the temperature. The piezoelectric coefficient (d₃₃) of the compound was recorded on the poled sample (4kV/cm for 4h in silicone oil) using a piezometer (M/s. Piezo-test, Model: PM 200, London). The polarization (hysteresis loop) of the poled sample was obtained at room temperature using Precision Material Analyzer (M/s. Radiant Technologies inc., NM, USA) integrated with 4kV voltage amplifiers.

3. Results and discussion 3.1 Thermal Analysis

The variation of mass and thermal parameters with temperature of mixture is shown in thermal gravimetric analysis (TGA) and differential thermal analyzer (DTA) curves [inset Fig. 1]. From TG curve of the above compound it is found that the first mass loss of about 4 % occurs in the temperature range of 50-200 0 C which occurs due to the evaporation of residual water that corresponds to an endothermic peak in the DTA curve. The second mass loss occurs (in two stages) in the temperature range of 200-400 0 C, which occurs due to intermediate reaction stage. In the third stage, the mass loss occurs at slower rate in the temperature range of 400-725 0 C which is due to evolution of CO₂ from the precursor materials. The nonexistence of mass loss and peaks beyond 725 0 C, suggests completion of reaction with the formation of compound.

3.2. Structure analysis

The room temperature XRD pattern of the calcined powder of $Li_2Pb_2Eu_2W_2Ti_4V_4O_{30}$ is shown inFig.1.The sharp and single diffraction peaks which are quite different from that of ingredients, confirmed the formation of a new single-phase compound [19].All the XRD peaks were indexed thoroughly using computer software "POWDMULT" [20]. Based on the best agreement between observed (obs) and calculated (cal) interplanerdistance d (i.e., Σ (d_{obs} -d_{cal}) = minimum), an unit cell of orthorhombiccrystal structure having lattice parameters: a = 19.5019(8) A °, b = 19.1706 (8) A °, c = 3.7974 (8) A ° (withestimated error in parenthesis) and volume (V) = 1419.71 (Å³) was selected. The unit cell parameters and crystal system of the compound matches with those reported earlier [16]. Table 1 compares the observed and calculated values of d of each reflection. The average crystallite size (P) of the compound was

determined from the broadening of a few XRD peaks using the Scherrer's equation: $P_{hkl} = \frac{\kappa\lambda}{\beta_{1/2} \cos \theta_{hkl}}$ [18], where k

(constant) = 0.89, λ =1.5405⁰A and $\beta_{1/2}$ = full width at half maximum (in radians). Due to use of powder samples for XRD pattern, reflection broadenings due to mechanical strain, instrumental, beam divergence, etc has been ignored for calculation of crystallite/particle size. The particle size was found to be about 30 nm.

3.3. Microstructure

Fig. 1(in set) shows the SEM micrograph of the compound at room temperature. The nature of microstructure (Shape, size and distribution of grains) of the sample confirmed the polycrystalline nature of the material with the plate like grains of size in the range 1-7 μ m. The grains are homogenously distributed over the entire surface of the sample with inter-grain porosity.

3.4. Dielectric study

Figure 2, shows the temperature variation of relative dielectric constant (ε_r) and loss tangent (tan δ) of the compound at four different frequencies (1, 10, 100 kHz and 1 MHz). From the graph it is observed that the relative dielectric constant increases gradually on increasing temperature, and reaches its maximum value (ε_{max}) at 404K after which it decreases. The above dielectric anomaly (known as transition temperature, T_c) is assumed to be related to a ferroelectric-paraelectric phase transition which was later confirmed by polarization study. Above T_c, the increase of ε_r (at lower frequency i.e at 1 kHz) may be due to space charge polarization which arises due to imperfections in the material and mobility of ions. Due to the above reason there is a sharp increase in the ε_r with increasing temperature. The maximum values of dielectric constant at T_c (i.e., ϵ_{max}) for 1, 10, 100 kHz and 1 MHzare 226, 131,102 and 88 respectively. The transition temperature (T_c) is independent of frequency, suggesting that the compound does not show any relaxor behavior. The variation of tand with temperature is different to that of ε_r . Though there is single phase transition in the compound, two peaks are observed in the plot temperature vs. loss tangent. The first peak in tand occurs at about 373 K and second peak is observed at 528 K. In diffused phase transition, the dielectric constant and loss peaks occurat different temperatures with separation depending upon he degree of broadening of the peaks, and the temperatured pendence of the dielectric relaxation [21]. The higher value of $tan\delta$ at high temperature may be due to space charge polarization and reduction in ferroelectric domain wall contribution. Both the dielectric constant (ε_r) and dielectric loss (tan δ) decrease on rising frequency, which indicates a normal behavior of polar dielectrics [22].

The width of the dielectric peaks increases with increasing frequency which is an indication of diffuse phase transition in the material. The degree of diffuseness at the peak is calculated using a general expression: In $(1/\varepsilon_r - 1/\varepsilon_{max}) = \ln (T - T_c) + constant$ [23], where the symbols have their usual meaning. The value of diffusivity (γ) , calculated from the slope of In $(1/\varepsilon_r - 1/\varepsilon_{max})$ vs. In $(T - T_c)$ plots (Fig. 3), at 10 kHz was found to be 1.03. The value $(1 < \gamma < 2)$ clearly suggests the existence of diffuse phase transition in the material. The complex and disordered system like TB – ferroelectrics usually show diffuse phase transition which is due to the presence of some non-equivalent positions in the unit cell [24].

3.5 Polarization study

The variation of electrical polarization with electric field at room temperature (hysteresis loop) of the sample was shown in Fig. 4, which confirms the ferroelectric properties in the material. The retentivity $(2P_r)$ and coercive field (E_c) was calculated to be 0.148μ C/cm² and 3.08kV/cm respectively. The piezoelectric coefficient (d₃₃) of poled sample was found to be 5pC/N. This value of the compound was found to be very small as compared to other ferroelectric oxides (i.e., BaTiO₃, PZT, PLZT, PMN, etc.).

3.5 Complex Impedance analysis

Complex impedance spectroscopy (CIS) is an effective technique to study the electrical response of ionic and polycrystalline materials. The intra-grain, inter-grain and other electrode effects are usually responsible for the electrical properties of ferroelectric materials. We need to separate grain, grain boundary and electrode contributions in the material in order to know the contributions of these effects to the electrical properties of a sample. CIS is a wonderful and very powerful tool to separate out these contributions. Some important data having both real (resistive) and imaginary (reactive) components are provided by the measurements of impedance and related parameters of the materials. Using the below given formulas we can calculate these components: complex impedance $Z(\omega) = Z' - jZ'' = R_s - \frac{j}{\omega C_s}$, complex electrical modulus $M(\omega) = \frac{1}{\epsilon(\omega)} = M' + j M'' = j \omega CoZ$, complex admittance $Y^* = Y' + jY'' = j\omega C_0 \epsilon^* = (R_p)^{-1} + j\omega C_p$ and complex permittivity $\epsilon^* = \epsilon' - j\epsilon''$ where ω

= $2\pi f$ is the angular frequency; C₀ is the geometrical capacitance, j = $\sqrt{-1}$ and subscripts p and s are parallel and series circuit components respectively.

The frequency dependence of Z' and Z'' at different temperatures is shown in Fig. 5. The decrease of Z' value with increase in frequency and temperature indicates the rise of ac conductivity with an increasing temperature and frequency. At high frequency Z' of each temperature coincides with each other. This indicates the lowering of barrier properties of the sample with temperatures and then the disappearance of spacecharge would enhance the conductivity and reduce the impedance properties.

The variation of Z" with frequency reaches a maximum value (Z''_{max}) at all measured temperatures and the magnitude of Z"max decreases with increasing temperature indicating a decrease in the resistive property of the This confirms the existence of relaxation in the system [26]. The value of Z''_{max} shifts to higher material. frequencies with increasing temperature. A typical peak broadening which is asymmetric in nature with increase in temperature is observed which manifests the temperature dependent electrical relaxation phenomenon in the compound [27]. The relaxation process usually arises due to the presence of immobile charges at low temperature and defects/vacancies at higher temperatures. The high frequency slopes are independent of temperature. Otherwise, low frequency slopes strongly depends on temperature. As two temperature dependent slopes are observed in the material, it confirms two distinct dispersion mechanisms in it. The complex impedance spectra (Nyquist plot) with fitted data [28] of the material at selected temperatures (>350^oC) over a wide frequency range (1 kHz to 1 MHz) is plotted in Figure 6.The plot shows semicircular arcs. At low temperatures, complex impedance plots are single semicircular arc (which is not shown in figure) whereas, at higher temperature $(375^{\circ}C \text{ and above})$ two semicircular arcs with center below real axis are observed. The nature of plots shows that the electrical response is composed of at least two semi-circles, first due to bulk (grain) property of material whereas the second one (at high temperature) is due to the presence of grain boundary [29]. All the semicircles exhibit some depression instead of a semicircle centered on the Z'-axis. Such a behavior is an indication of non-Debye type of relaxation and it reveals the distribution of relaxation time instead of a single relaxation time in the material [30]. From fitting curves, the calculated value of bulk resistance (R_b) and grain boundary resistance (R_{gb}) at different temperatures are compared in Table 2. It is clearly observed that both the parameters decrease with rise in temperature showing the negative temperature coefficient resistance (NTCR) behavior of the material.

Fig .7 shows the reactive part of impedance (Z'') and modulus (M'') spectroscopy. It was reported by Sinclair and West [31], that the combine plot of Z'' and M'' as a function of frequency is used to detect the presence of

smallest capacitance and largest resistance. According to Sinclair and West if peaks of Z" and M" occur at different frequencies then motion of charge carrier is short range whereas for long range movement of charge carrier peaks occur at same frequencies. The existence of peaks at different temperature manifests the short range motion of charge carrier and departure from ideal Debye-like behavior in the compound[32].

Fig. 8 shows the variation of $\ln \tau_b$ with inverse of absolute temperature $(10^3/ \text{ T})$. The value of τ_b decreases with rise in temperature, and thus temperature dependent relaxation time for bulk follows the Arrhenius relation: $\tau_b = \tau_o \exp(-E_a / K_B T)$ 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 1.64eV which consistent with reported one [18].

3.6 Complex Electric Modulus Analysis

Electrical modulus studies can be used to detect electrode polarization, grain boundary conduction effects, bulk properties, electrical conductivity, and the relaxation process [33]. Fig 9 shows the variation of M' with frequency at selected temperatures. In the low-frequency region, the magnitude of M' tends to zero, and thus coincide with each other, which confirms a negligibly small contribution of electrode effect.

The value of M' increases and reaches a constant value at higher frequencies. Such observation may possibly be related to a lack of restoring force governing the mobility of the charge carriers under the action of an induced electric field. This behavior supports the long-range mobility of charge carriers [34]. In the frequency-temperature dependence of imaginary part of electric modulus (M") plot (Fig.9 inset), M"_{max} shifts towards higher relaxation frequencies with a rise in temperature. This behavior suggests that dielectric relaxation is thermally activated in which the hopping mechanism of charge carriers dominates intrinsically [34]. Asymmetric broadening of the peak indicates a spread of relaxation with different time constants, and hence the relaxation in the material is of a non-Debye type. The scaling behavior of the sample was studied by plotting normalized parameters (i.e., M"/M^{max}_{max}vers log (f/f_{max}) where f_{max} corresponds to a value of M^{max}_{max} at different temperatures (Fig.10). This curve gives an insight into the dielectric processes occurring inside the material as a function of temperature. The coincidence of the curves at different temperature indicates the temperature independent behaviour of dynamic processes occurring in

the material [34]. This may be due to charge carrier migration by hopping mechanism. The frequency region where the peak occurs indicates the transition from long range to short range mobility (on increasing frequency) [35].

3.7. AC Conductivity

The variation of electrical conductivity $\sigma_{ac}(\omega)$ with frequency at different temperatures is shown in Figure 11. The conductivity is found to be increasing with increase in frequency and temperature. The conductivity is less at low frequencies because, at these frequencies, the mobility of charge carriers is less due to less concentration of oxygen vacancies. At high frequencies there is a tendency of merger of conductivity curves and hence dispersion becomes temperature and frequency independent. With increase in temperature, the conductivity response become more and more flattened in low frequency and high temperature region which may be due to transition from long range hoping to short range ionic motion, and thus conductivity relaxation phenomena [36, 37] occurs. The ac conductivity with frequency graph is fitted with Jonscher's power law relation: $\sigma_{ac} = \sigma_{dc} + A\omega^n$, where σ_{dc} is the dc conductivity (frequency independent plateau in the low frequency region), A is the temperature dependent frequency preexponential factor and n is the power law exponent in the range of $0 \le n \le 1$. The exponent n represents the degree of interaction between mobile ions with the lattice around them, and the pre exponential factor A determines the strength of polarizability. The material obeys the universal power law, and is confirmed by a typical fit of the above equation to the experimental data at various temperatures. When a mobile charge carrier hops to a new site from its original position, it remains in a state of displacement between two potential energy minima. From non-linear fitting it is found that the motion of charge carriers in the samples is translational one because of small value of n (<1) [38]. The dc conductivity increases with rise in temperature (as expected) in the given material. The temperature dependence of dc conductivity, A and n has been compared in Table 3.

3.8 DC Conductivity

Figure 12 indicates the variation of dc conductivity with respect to inverse of absolute temperature. The bulk conductivity of the material was evaluated from the complex impedance plots of the sample using the relation: $\sigma_{dc} = t / R_b A$, 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 which confirms the negative temperature co-efficient of resistance

(NTCR) behavior. This plot follows the Arrhenius relation: $\sigma_{dc} = \sigma_0 e^{-\frac{E_a}{K_BT}}$. The activation energy value estimated from the conductivity variation pattern was found to 1.4 eV which is quite different from the value estimated from the relaxation time plot. This implies that the charge carriers responsible for conduction and relaxation are different.

4. Conclusion

The polycrystalline sample of $Li_2Pb_2Eu_2W_2Ti_4V_4O_{30}$ was synthesized by a low temperature solid state reaction route. X-ray analysis confirms the orthorhombic crystal structure of the compound at room temperature. A dielectric peak at 404K has been observed, which suggests the ferroelectric–paraelectric phase transition, which is confirmed by appearance of hysteresis loop at room temperature. Complex impedance analysis (CIS), studied the electrical behavior and the presence of both grain and grain boundary effects in the material. Modulus analysis reveals non-exponential type of conductivity relaxation in the material. The ac conductivity obeys the universal power law and the dispersion in conductivity has been observed in the lower frequency region. The variation of dc conductivity (bulk) as a function of temperature suggests that the compound has Arrhenius type of electrical conductivity and NTCR behavior like semiconductor.

5. References

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Figure Captions:

Fig.1 Indexed XRD pattern, TGA and DTA curves and SEM of LPEWTV.

Fig.2 Variation of relative dielectric constant with temperature as well as Tangent loss with temperature of LPEWTV.

Fig.3. Variation of $\ln[1/\epsilon_r - 1/(\epsilon_r)_{max}]$ with $\ln(T - T_c)$ of LPEWTV at 10 kHz.

Fig.4. Hysteresis loop of LPEWTV at room temperature.

Fig. 5. Variation of Z' and Z'' with frequency of LPEWTV

Fig.6 Variation of Z with Z of LPEWTV.

Fig. 7. Variation of M" and Z" with frequency at different temperatures of LPEWTV.

- Fig. 8.Variation of relaxation time (τ) as a function of reciprocal of absolute temperature Of LPEWTV.
- Fig.9. Variation of M' and M" with frequency at different temperatures of LPEWTV.
- Fig.10. Variation of, M''/M''_{max} with log (f/f_{max}) at different temperatures of LPEWTV.
- Fig.11. Variation of ac conductivity with frequency at different temperatures of LPEWTV.
- Fig.12.Variation of dc conductivity (obtained from impedance pattern) as a function of temperature of LPEWTV.

Table Captions:

Table 1 Comparison of d_{obs}and d_{eal} for different h k l plane with intensity ratio Table 2 Comparison of bulk (grain) and grain boundary resistance and capacitance at different temperatures

Table 3 Comparison of σ_{dc} , A and n at different temperature.

Table 1 Comparison of d_{obs} and d_{cal} values of all the reflections of XRD peaks

Sl.No	d_{obs}	d_{cal}	I/I ₀	h k l
1	3.6099	3.6127	25	520
2	3.2326	3.2320	100	3 1 1
3	2.9985	2.9959	24	4 0 1
4	2.8678	2.8675	10	3 6 0
5	2.7064	2.7062	42	3 4 1
6	2.5537	2.5538	13	7 3 0
7	2.4793	2.4793	13	6 5 0
8	2.3779	2.3784	11	1 8 0
9	2.2883	2.2883	10	3 6 1
10	2.2483	2.2484	12	3 8 0
11	2.1856	2.1854	11	4 6 1
12	2.0145	2.0157	43	1 8 1
13	1.9178	1.9171	26	0 10 0
14	1.8542	1.8541	27	1 2 2
15	1.8040	1.8054	15	9 3 1
16	1.7730	1.7729	32	11 0 0
17	1.6851	1.6856	20	2 10 1
18	1.6513	1.6512	47	6 10 0
19	1.6161	1.6160	32	6 2 2
20	1.5003	1.5001	18	13 0 0
21	1.4547	1.4548	16	12 3 1
22	1.4084	1.4083	14	7 6 2
23	1.3570	1.3570	20	10 1 2
24	1.3126	1.3126	23	782
25	1.3037	1.3037	30	9 6 2
26	1.2510	1.2509	20	11 4 2
27	1.2362	1.2363	19	4 15 0
28	1.2153	1.2153	20	4 2 3
29	1.2043	1.2043	15	14 8 0

Table 2 Comparison of bulk (grain) and grain boundary resistance and capacitance at different

	temperatures						
Temperature(⁰ C)	R _b (in ohm)	Cb(in F)	CPE	l(Q) n	Rgb(in ohm)	Cgb(F)	
325	7.816E54.70	64E-116.197E-9	0.54				
350	5.322E55.35	51E-111.613E-8	0.45				
375	1.741E5	3.679E-111.04	43E-9	0.743.6E4	4 1.271E-8		
400	5.674E4	6.259E-11 3.83	3E-7	0.28 882	51.79E-10		
425	2.59E4	5.741E-111.77	6E-6	0.21 572.	1 1.036E-10		

Temperature (°C)	σ_{dc} (ohm ⁻¹ m ⁻¹)	А	n
200	0.00001	3.1835E-8	0.681
225	0.00003	2.5973E-8	0.709
250	0.00004	1.9848E-8	0.744
350	0.00006	1.5636E-8	0.790
375	0.00012	2.2455E-8	0.783
400	0.00041	3.843E-7	0.596

Table. 3 Comparison of $\sigma_{\text{dc}},$ A and n at different temperatures.



Fig.1



Fig. 2



Fig.3



Fig.4



Fig.5













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