

Structural and dielectric properties of $\text{Dy}_2(\text{Ba}_{0.5}\text{R}_{0.5})_2\text{O}_7$ (R = W, Mo) ceramics

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ABSTRACT

The polycrystalline samples of the pyrochlore-type $\text{Dy}_2(\text{Ba}_{0.5}\text{R}_{0.5})_2\text{O}_7$ (R = W, Mo) compounds have been prepared by a high-temperature solid-state reaction technique. Preliminary X-ray diffraction (XRD) studies and scanning electron micrographs (SEM) of the compounds at room temperature suggested that compounds have single phase orthorhombic crystal structures and grain distribution throughout the surface of the samples was uniform. Dielectric studies (dielectric constant (ϵ') and tangent loss ($\tan \delta$) obtained both as a function of frequency (4 kHz-1 MHz) at room temperature (RT) and temperature (RT 320 °C) at 20 kHz and 100 kHz suggest that compounds do not have dielectric anomaly in the said frequency and temperature range. Copyright © 2010 VBRI press.

Keywords: Dielectrics; electrical properties, X-ray diffraction, scanning electron micrographs



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Introduction

With the growing interest in the suitability of materials for device applications, a large number of ceramics have been developed in a wide variety of compositions and stable structure. Visible light photo-degradation phenomena are not limited to titanium dioxide. In fact other oxides, and in particular mixed oxides such as $\text{A}_2\text{B}_2\text{O}_7$ compounds are often considered to have photocatalytic properties. Luan et.al [1-2], studied the $\text{Bi}_2\text{InTaO}_7$ crystallizes with the pyrochlore-type structure, which acts as a photocatalyst under visible light irradiation and seems to have potential for activity improvement upon modification of its structure. They also reported that Gd_2YSbO_7 and $\text{Gd}_2\text{BiSbO}_7$ are semiconductor compounds. The similarity between the molecular composition of these two compounds and other

$A_2B_2O_7$ compounds suggests that these two compounds may possess photocatalytic properties under visible light irradiation and may be to those of other members of the family. Some oxides of the pyrochlore structure-type exhibit a variety of potentially useful properties, which include catalysis, ferroelectricity, luminescence and ionic conductivity [3-5]. The ionic conductors have various types of skeleton structure which provide a pathway for mobile ions. Fluorite (F)-type oxides having high potential for oxide-ion conductors can accept various amounts of oxygen vacancy, from which a pyrochlore-type (P) structure can be derived. Although pyrochlore structures are widely used for active and passive electronic devices, such as switching elements, thick-film resistors, and materials for screen printing, they have been recognized only recently as potential candidates for temperature-stable, low-loss, high-permittivity dielectric applications [6-9]. In addition to these promising properties, the proposed system can be sintered at low temperature (950°C), which makes them viable as cofired dielectric components. The P-type structure which has a general composition $A_2B_2O_7$ can be considered as an order defect F-type structure with space group $Fd\bar{3}m$ ($Z=8$), keeping a cubic symmetry. In $A_2^{3+}B_2^{4+}O_7$ system, the rare earth ion A^{3+} is located at the 16c site, B^{4+} ion at 16d site and O^{2+} at 8a and 48f site of the structures respectively [10-11]. Some pyrochlore compounds are intrinsic oxide conductors and have potential use in solid-oxide fuel cells [12,13]. In this paper we report our preliminary structural and dielectric properties of $Dy_2(Ba_{0.5}R_{0.5})_2O_7$ ($R = W, Mo$) compounds.

Experimental

The polycrystalline samples of $Dy_2(Ba_{0.5}Mo_{0.5})_2O_7$ (A) and $Dy_2(Ba_{0.5}W_{0.5})_2O_7$ (B) were prepared from high purity $BaCO_3$ (M/S Burgoyne Buirbridger, India), Dy_2O_3 (M/S Indian rare earth Ltd.), and WO_3 (M/S John Baker Inc., USA), MoO_3 , (M/s. Loba Chemie Pvt. Ltd., India) using a high-temperature solid-state reaction technique. These materials were taken in a suitable stoichiometry ratio and mixed thoroughly with methanol in an agate-mortar for 2 h. The mixtures of ingredients of compounds A and B were calcined in an alumina crucible at 1000 °C for ~12 h in air atmosphere. The process of grinding calcinations was repeated thrice for formation of the compounds. The final calcination was done at 1120 °C for ~10 h in air atmosphere. The fine powders of A and B mixed with the binder, polyvinyl alcohol (PVA) were compacted into cylindrical discs (pellets) of diameter ~10 mm and thickness 1-2 mm at the pressure of 5×10^7 N/m² using a hydraulic press. The pellets of A and B were sintered in air at 1220 °C for 10 h in high purity alumina crucibles. The formation and quality of the compounds were checked with X-ray diffraction (XRD) technique. The X-ray diffraction pattern of the compounds was recorded at room temperature using X-ray powder diffractometer with CuK_{α} radiation ($\lambda = 1.5418\text{\AA}$) in a wide range of Bragg angles 2θ ($20^\circ \leq 2\theta \leq 80^\circ$) at a scanning rate of 2°min^{-1} . Scanning electron microscope (SEM) micrographs of the pellets specimens were acquired with the help of a JEOL-JSM-5800 scanning electron microscope. The flat polished surface of sintered pellets were electroded with air drying

silver paste and fired at 150°C for 2 h before taking any electrical measurement.

The dielectric constants (ϵ'), loss tangent ($\tan \delta$) and ac conductivity of samples were measured as a function of frequency at room temperature and temperature (30–320°C) at two different frequencies (20 and 100 kHz) using a HIOKI 3532 LCR Hi-tester meter (Japan) with a laboratory-made three-terminal sample holder. All the measurements were recorded in small temperature intervals (~2°C) from room temperature to 320°C.

Results and discussion

The sharp and single diffraction peaks of the polycrystalline compounds indicate homogeneity and crystallization of the samples. Fig. 1(a) & 1(b) confirmed the formation of the single phase compounds. All the reflection peaks were indexed in different crystal systems and configurations using observed interplanar spacing d , and lattice parameters of samples were determined. The selected lattice parameters were refined using a least squares refinement method of a computer program package 'PowdMult' [14]. Finally, a unit cell of orthorhombic crystal system was selected for which $\Sigma\Delta d = (d_{\text{obs}} - d_{\text{cal}})$ was found to be minimum (Standard deviation is 0.002). The least-squares refined parameters for A and B compounds are given in Table 1.

Table 1. Comparison of some observed (obs) and calculated (cal) d -values (in nm) of some reflections of $Dy_2(Ba_{0.5}Mo_{0.5})_2O_7$ and $Dy_2(Ba_{0.5}W_{0.5})_2O_7$ at room temperature. The estimated error in d is ± 0.00010 nm.

h	k	l	d_{obs}	d_{cal}	I/I_0
$Dy_2(Ba_{0.5}Mo_{0.5})_2O_7$					
1	0	3	4.3533	4.3523	12
1	0	4	3.3510	3.3675	97
0	2	2	3.1978	3.1859	17
1	2	2	2.0737	3.0742	100
2	1	4	2.7841	2.7776	21
4	1	1	2.6633	2.6611	23
2	3	2	2.1034	2.1057	25
0	3	4	1.9730	1.9723	9
6	1	0	1.8843	1.8835	35
6	2	1	1.7110	1.7008	18
2	2	7	1.6794	1.6779	11
5	2	5	1.6079	1.6078	23
5	3	3	1.5328	1.5736	11
5	1	1	1.1394	1.3888	5
$Dy_2(Ba_{0.5}W_{0.5})_2O_7$					
3	1	1	3.3023	3.3017	100
1	2	2	3.0279	3.0268	73
4	0	0	2.9122	2.9108	21
0	0	5	2.7757	2.7731	29
4	1	1	2.6405	2.6394	27
5	1	2	2.1057	2.1057	31
5	1	3	1.9935	1.9938	18
3	2	5	1.8935	1.8976	31
1	4	1	1.7202	1.7209	28
6	2	0	1.6981	1.6980	18
1	3	6	1.6287	1.6276	20
5	2	7	1.3858	1.3860	11
1	0	10	1.3768	1.3768	15
2	3	9	1.2564	1.2562	9

The linear particle size (P_{hkl}) of both the samples were calculated from some strong and medium intensity peaks using Scherrer's equation [15] $P_{hkl} = 0.89 \lambda / \beta_{1/2} \cos \theta_{hkl}$, where λ is the wavelength of X-ray radiation, $\beta_{1/2}$ the width at half maximum of the diffracted peak and θ_{hkl} the angle of diffraction. The SEM micrographs of the A and B compounds at room temperature are shown in inset of Fig. 1(a) & 1(b). It was found that the grains are homogeneously distributed over the entire surface of samples.

Fig. 2 shows the frequency (4 kHz - 1 MHz) dependence of relative dielectric constant (ϵ') and tangent loss ($\tan \delta$) (inset) at room temperature ($\sim 30^\circ\text{C}$) of both the compounds. It has been observed that the values of the dielectric constant (ϵ') and tangent loss ($\tan \delta$) of the above compounds decrease with increasing frequency indicating a normal behavior of dielectrics/ferroelectrics [16]. The trend in $\tan \delta$ versus frequency curve might be attributed to parallel conduction ($\tan \delta_p = 1/\omega CR$, where ω is the angular frequency, C the capacitance and R is the resistance), which is probably due to porosity. It is observed that at higher frequencies this parameter becomes almost frequency-independent.

Fig. 3 shows the variation of ϵ' for A and B compounds with temperature (30–320°C) at frequencies 20 kHz and 100 kHz. For A compound the value of ϵ' increases with rise in temperature but rate of increase was much faster upto 100 °C then remains almost constant in the temperature region 98 to 261°C. For B compound dielectric constant (ϵ') increases slowly up to temperature 118°C then remains almost constant up to 212°C. The variation of tangent loss ($\tan \delta$) for A and B compounds with temperature (30–320°C) at frequencies 20 kHz and 100 kHz are shown in Fig. 3 (in inset). In case of a compound the value of $\tan \delta$ increases with rise in temperature. Similar increasing trend at higher temperature ($>270^\circ\text{C}$) was observed in B compound. Tangent loss ($\tan \delta$) increases slowly at 20 kHz and 100 kHz but at higher temperature ($>300^\circ\text{C}$) rate of increase were much faster at 20 kHz than 100 kHz in B compounds.

The variation of measured ac conductivity ($\ln \sigma_{ac}$) of the A and B compounds at 20 and 100 kHz with inverse of absolute temperature ($1/T$) is shown in Fig. 4. The temperature dependence of ac electrical conductivity σ_{ac} and activation energy (E_a) of the A and B compounds were calculated by using the formula [17, 18]

$$\sigma = \omega \epsilon_0 \epsilon' \tan \delta$$

$$\text{and } \sigma = \sigma_0 \exp(-E_a/KT)$$

where ω is the angular frequency, ϵ_0 is the vacuum permittivity and K is the Boltzmann constant. The value of the activation energy E_a has been calculated from the slope of the graph in high temperature region ($>280^\circ\text{C}$) and was found to be 0.120 eV for A compound and 0.008 eV for B compound at 100 kHz. The low values of activation energy were supported the superionic nature of the compounds in the high temperature region. In both the compounds conductivity at higher temperature is higher, which is common behavior of most of the dielectric ceramics.

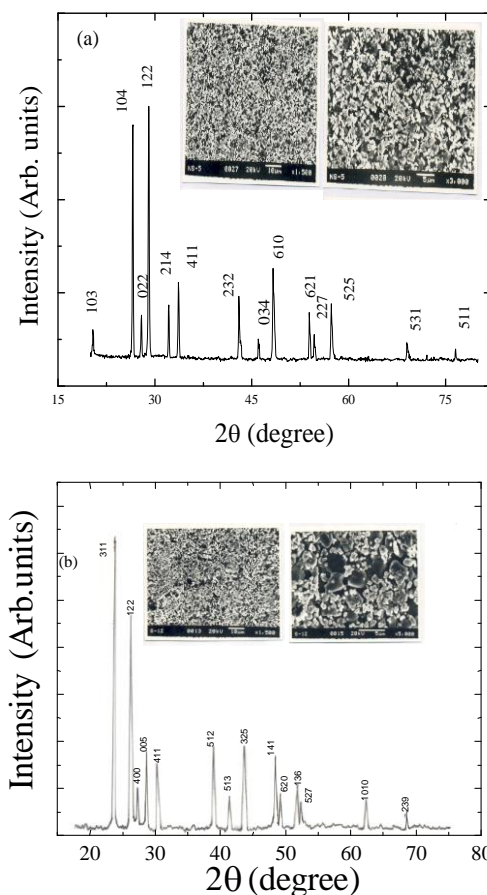


Fig. 1. (a) XRD pattern of $\text{Dy}_2(\text{Ba}_{0.5}\text{Mo}_{0.5})_2\text{O}_7$ samples at room temperature and SEM micrographs (in inset) at 5 μm and 10 μm magnification of $\text{Dy}_2(\text{Ba}_{0.5}\text{Mo}_{0.5})_2\text{O}_7$ and (b) XRD pattern of $\text{Dy}_2(\text{Ba}_{0.5}\text{W}_{0.5})_2\text{O}_7$ samples at room temperature and SEM micrographs (in inset) at 5 μm and 10 μm magnification of $\text{Dy}_2(\text{Ba}_{0.5}\text{W}_{0.5})_2\text{O}_7$.

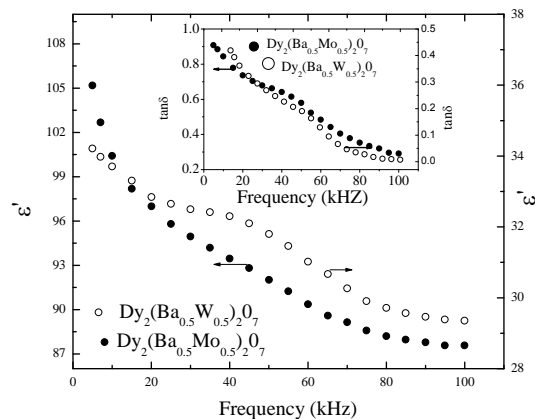


Fig. 2. Variation of relative dielectric constant (ϵ') of $\text{Dy}_2(\text{Ba}_{0.5}\text{W}_{0.5})_2\text{O}_7$ and $\text{Dy}_2(\text{Ba}_{0.5}\text{Mo}_{0.5})_2\text{O}_7$ and variation of tangent loss ($\tan \delta$) of $\text{Dy}_2(\text{Ba}_{0.5}\text{W}_{0.5})_2\text{O}_7$ and $\text{Dy}_2(\text{Ba}_{0.5}\text{Mo}_{0.5})_2\text{O}_7$ with frequency at room temperature (inset).

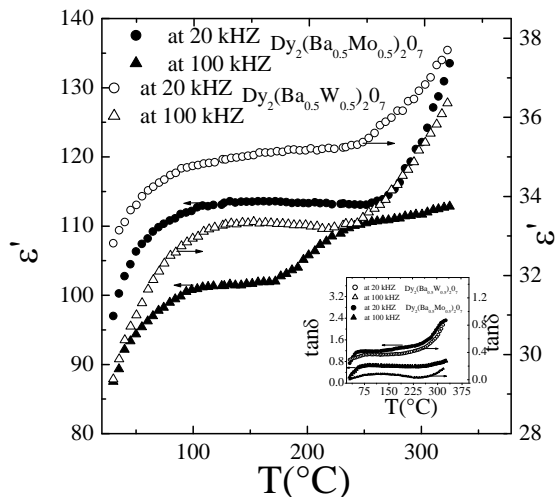


Fig. 3. Variation of dielectric constant (ϵ') and tangent loss ($\tan \delta$) (in inset) as a function of temperature at 20 and 100 kHz of $\text{Dy}_2(\text{Ba}_{0.5}\text{W}_{0.5})_2\text{O}_7$ and $\text{Dy}_2(\text{Ba}_{0.5}\text{Mo}_{0.5})_2\text{O}_7$ samples respectively.

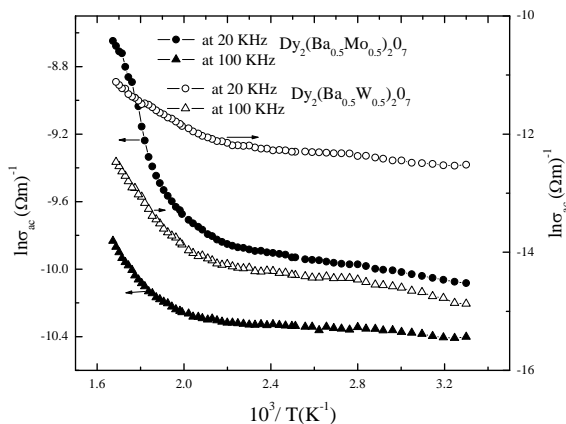


Fig. 4. Variation of ac conductivity ($\ln \sigma_{ac}$) of $\text{Dy}_2(\text{Ba}_{0.5}\text{W}_{0.5})_2\text{O}_7$ and $\text{Dy}_2(\text{Ba}_{0.5}\text{Mo}_{0.5})_2\text{O}_7$ with inverse of absolute temperature at frequencies 20 and 100 kHz.

Conclusion

Finally, it can be concluded that the compounds **A** and **B** have orthorhombic structure at room temperature. Studies of the dielectric constant (ϵ') and tangent loss ($\tan \delta$) of compounds as a function of frequency (4 kHz – 1 MHz) at room temperature and (30–320°C) suggest that the compounds do not have dielectric anomaly in the said frequency and temperature range. The low values of activation energy were supported the superionic nature of the compounds in the high temperature region.

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