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Structural and electrical properties of Mg_2TiO_4

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We have studied the structural and electrical properties of Mg_2TiO_4 inverse spinel using X-ray diffraction, Raman spectroscopy, ac conductivity and dielectric spectroscopy. Polycrystalline sample of Mg_2TiO_4 was prepared by the conventional solid state reaction technique. Powder X-ray diffraction analysis indicates single phase nature of inverse spinel Mg_2TiO_4. Raman study also infers that Mg_2TiO_4 exhibits inverse spinel structure. The dielectric constant measured as a function of frequency exhibits a resonance peak at 9 MHz. The dielectric constant measured as function of temperature (100–300 K) at 500 kHz is found to increase with temperature. The value of the loss tangent (tanδ) was found to be small ~ 0.01 through out the whole temperature range. The value of the exponent (s), evaluated using the power law $\sigma_{AC} = \omega^S$, is found to be ~1, which indicates the good correlation of the hoping of carriers in the system.

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1. Introduction

During the last few years there has been resurgence of interest in the study of spinel oxides AB_2O_4 due to its variety of physical properties and advanced technological applications.[1] The spinel oxides are one of the richest families showing the number of compounds and diversity of observed physical properties such as ferromagnetic ordering, metal-insulator transition, heavy fermion behavior, charge ordering, superconductivity[2)–10)] etc. The invention of the high temperature superconductivity in cuperates regenerates the study on transition metal oxides to understand the electronic structure and the effect of the disorder on the electronic correlation effect. Out of more than 300 transition-metal ternary compounds of the spinel structure, only few, specifically $LiTi_2O_4$, CuV_2S_4, $CuRh_2S_4$ and $CuRh_2Se_4$ are recognized to be superconductors.[11),12)] It is also observed that materials with high dielectric constants have also fascinated much interest due to their vast technological applications like wireless communication systems such as cellular phones and global positioning systems, namely as capacitors, resonators, or filters. High dielectric constants allow smaller capacitive components, thus offering the opening to decrease the size of electronic devices. Large number of investigators studied the Ti substituted spinel oxides in order to understand their electrical and magnetic properties.[13)–16)] As it is known from the literature survey that titanium substituted spinel shows a vast variety of physical properties. It is also found that the electrical properties of the spinel oxides are important not only from the application point of view, but also from the fundamental point of view. Moreover, the study of ac electrical conductivity sheds light on the behavior of the charge carriers under an ac field, their mobility and the mechanism of conduction.

From the literature, it is well known that the magnesium titanates are good candidate for use in the microwave dielectrics which could be used in the modern communication such as filters and oscillators as well as microwave components- dielectric resonator, dielectric substrate, wave guides and antennas. Mg_2TiO_4 can also be used as a novel substrate for epitaxial growth of the high temperature superconducting thin films.[17)] However, it is found from the literature survey that there is no report on the dielectric and ac electrical conductivity measurements of Mg_2TiO_4 system.

In this paper, we have studied the structural and electrical properties. The effect of frequency and temperature on the dielectric behavior of Mg_2TiO_4 has been discussed.

2. Experiment

Polycrystalline sample of inverse spinel Mg_2TiO_4 was synthesized using conventional solid-state reaction technique. The stoichiometric amount of highly pure $Mg(NO_3)_2{\cdot}6H_2O$, and TiO_2 powder were mixed thoroughly and pre-calcinated for 12 h at 1000°C. The pre-calcinated material was again ground and calcinated at 1250°C for 24 h. Finally, the sample was ground to fine powder, pressed to pellet form and sintered at 1300°C for 24 h and at the end of each heat treatment the sample was allowed to cool slowly to room temperature. Powder X-ray diffraction (XRD) was performed using Bruker AXE D8 X-ray powder diffractometer with Cu Kα radiation at room temperature and data was analyzed by Powder-X[18)] software. micro-Raman measurements were performed using a Renishaw Raman spectrometer working with an excitation wavelength of 514 nm from Ar ion laser. Dielectric measurements were performed using HP 4284A Precision LCR meter. For measuring the dielectric constant, pressed rectangular pellets of sample material was covered on adjacent faces with silver paint, thereby forming the parallel plate capacitor geometry. The dielectric measurements were performed from 75 kHz to 20 MHz. The value of the dielectric constant (ε') of Mg_2TiO_4 is calculated using the formula;

$$\varepsilon' = \frac{C \times t}{\varepsilon_0 \times A} \quad (1)$$

where ε_o is permittivity in vacuum equal to 8.854×10^{-12} $C^2/N{\cdot}m^2$,

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C is the capacitance of the specimen, t is the sample thickness and A is the area of the specimen in sq. m.

The a.c. conductivity of Mg_2TiO_4 is calculated using the relation

$$\sigma_{a.c.} = \varepsilon'\varepsilon_o\omega \tan\delta \quad (2)$$

where ε_o is the permittivity of vacuum and $\omega = 2\pi f$ and $\tan\delta$ is loss tangent which is proportional to the 'loss' of energy from the applied field on the sample (in fact this energy is dissipated into heat) and therefore denoted as dielectric loss.

3. Results and discussion

The XRD pattern of Mg_2TiO_4 at room temperature is shown in **Fig. 1**, exhibits single phase nature. XRD spectrum was indexed using Powder X[18] software shows that the system exhibits a cubic spinel structure with space group $Fd\bar{3}m$ and lattice constant 8.456 Å. These results are consistent with the earlier reported,[19] where they studied the structure refinement of Mg_2TiO_4 by time-of-flight neutron diffraction and confirmed that cubic Mg_2TiO_4 had a completely inverse spinel structure.

Raman spectroscopy is one of the powerful technique, which is able to detect the microscopic vibrations caused by the subtle distortion between the similar structures. In order to confirm the formation of Mg_2TiO_4, Raman spectra of the sample was measured at room temperature as shown in **Fig. 2**. Mg_2TiO_4 has an inverse cubic spinel structure belonging to the space group $O_h^7(Fd\bar{3}m)$.[19] The unit cell of the Mg_2TiO_4 consists of eight formulae unit ($Z = 8$), the smallest Bravais cell contains only 14 atoms ($Z = 2$). The Ti and Mg atoms occupy the tetrahedral (8a) and octahedral (16d) sites. The oxygen atoms are in (32e) site symmetry positions. The factor group analysis predicts the following mode in the spinel[20]:

$$A_{1g}\,(R) + E_g\,(R) + F_{1g} + 3F_{2g}\,(R) + 2A_{2u} + 2E_u + 4F_{1u}\,(IR) + 2F_{2u}$$

According to the analysis (after subtracting the acoustic and silent modes) one can expect 5 Raman ($A_{1g} + E_g + 3F_{2g}$) and 4 infrared ($4F_{1u}$) active modes. Experimentally in the present system we have observed all five Raman active modes at the ambient condition at room temperature as shown in Fig 2. In cubic spinel, the mode observed above 600 cm^{-1} usually corresponds to the motion of oxygen in the tetrahedral AO_4 group. So, the two peaks observed at 608 cm^{-1} and 698 cm^{-1} are considered to represent A_{1g} symmetry. The other low frequency modes are the characteristic of the octahedral site (BO_6). Therefore the change in the peak position of 608 cm^{-1} and 698 cm^{-1} and their broadening reflects the local lattice effect in the tetrahedral (AO_4) sublattice whereas the changes in peaks position and broadening at 211 cm^{-1}, 325 cm^{-1} and 477 cm^{-1} reflects the local lattice effects in the octahedral sublattice. Our results are similar to the earlier reported other groups.[20]

Figure 3(a) shows the frequency dependence of the dielectric constant of Mg_2TiO_4 measured in the frequency range from 75 kHz to 20 MHz at room temperature. In general, dielectric behavior observed in such type of materials can be explained with interfacial polarization predicted by the Maxwell–Wagner model[21] in agreement with Koop's phenomenological theory.[22] According to these models, the dielectric materials can be imagined as a heterogeneous structure consisting of well conducting grains separated by thin layer of poorly conducting grain boundaries. These grain boundaries could be formed during the sintering process either by superficial reduction or oxidation of crystallites in the porous materials as a result of their direct contact with the firing atmosphere. The grain boundaries dominate at lower frequencies, while grains dominate at higher frequencies. It can be clearly seen from Fig. 3(a) that initially the dielectric constant decreases up to 500 kHz indicates that carriers does not follow alternating field up to this frequency. Beyond this frequency, the dielectric constant has been found to increase with increase in the frequency up to a resonance peak at 9 MHz. At the resonance peak (9 MHz) the applied frequency becomes equal to that of the hopping frequency between the ions and therefore, a relaxation peak appears. After this relaxation peak, with further increase in the frequency the dielectric constant decreases and does not follow the alternation of the applied ac field and approaches to a flat region. Figure 3(b) shows loss tangent ($\tan\delta$) as a function of the frequency. It is observed that with the increase in the frequency loss tangent increases.

The ac conductivity shown in **Fig. 4**(a), evaluated from the data of dielectric measurements is also found to increase with increase in the frequency. The reason behind these phenomenons may be that during the synthesis process some vacancies may be established in system. Such vacancies may change the oxidation state of Ti ions (Ti^{4+} to Ti^{3+}), which in turns increases the number of electrons. Such mechanism will increase the hopping process and may account for the increase in the dielectric constant, $\tan\delta$

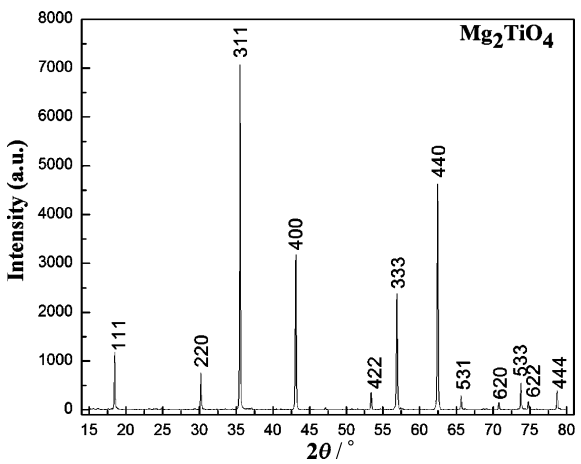


Fig. 1. Powder X-ray diffraction patterns of Mg_2TiO_4 at room temperature.

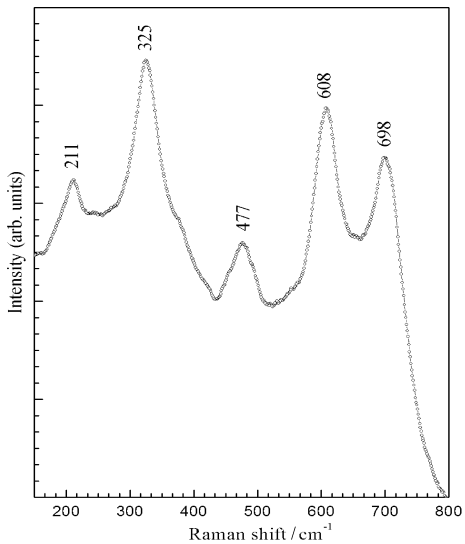
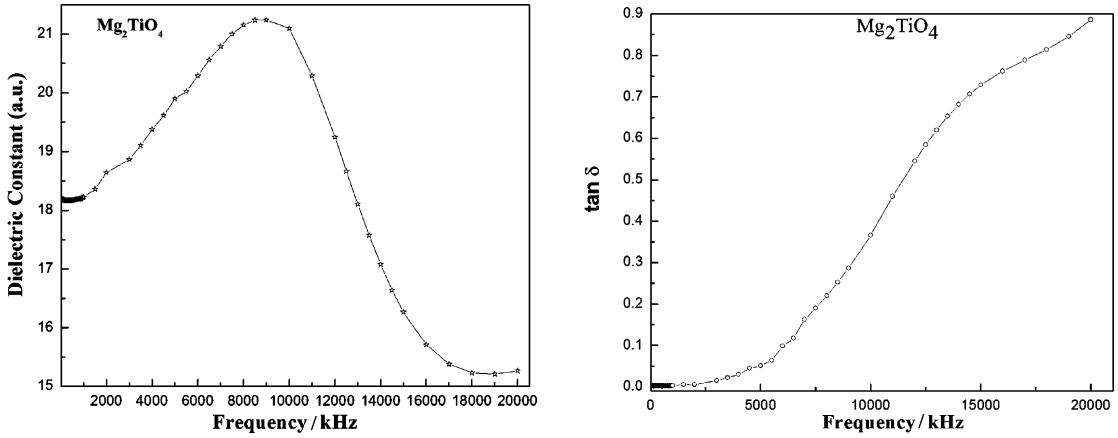
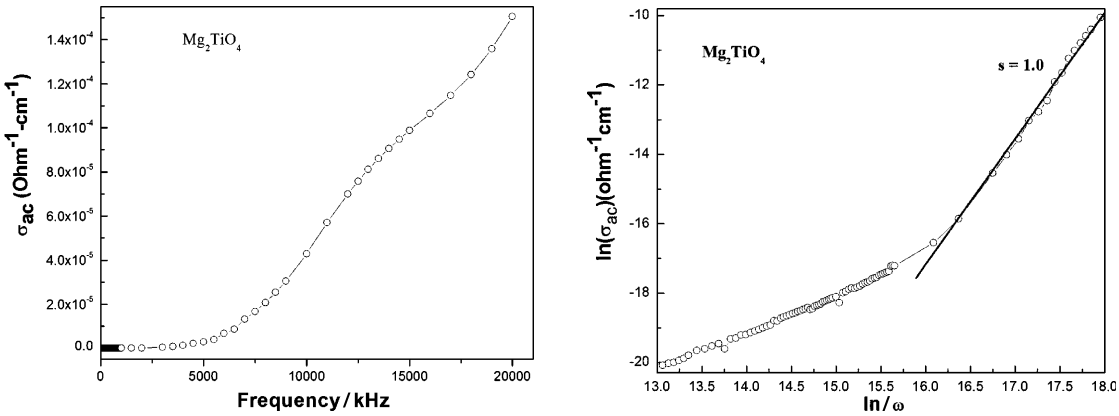


Fig. 2. Raman spectra of Mg_2TiO_4 at room temperature.



(a) (b)

Fig. 3. (a) Variation of dielectric constant as a function of frequency for Mg_2TiO_4; (b) Variation of loss tangent (tanδ) as a function of frequency for Mg_2TiO_4.



(a) (b)

Fig. 4. (a) Variation of ac conductivity ($\sigma_{a.c.}$) as a function of frequency for Mg_2TiO_4; (b) Variation of ln($\sigma_{a.c.}$) as a function of ln(ω) for Mg_2TiO_4.

and ac conductivity of the material. In general for oxide ceramic materials, the ac conductivity follows the power law behaviour with frequency given as;[23),24)]

$$\sigma_{AC} = A\omega^{s} \quad (3)$$

where A is a constant having the unit of the conductivity and the exponent s is a dimensionless parameter and ω is the angular frequency at which the conductivity was measured. In the present case, the exponent (s) was calculated at room temperature over the studied range of frequency by plotting ln σ_{AC} versus ln ω, according to Eq. (3) and is shown in Fig. 4(b). The exponent s is a measure of the degree of correlation, i.e., s should be zero for random hopping and tends to one as the correlation increases. In the present systems s values have been found ~1, which clearly indicates that there is strong correlations of carriers in the systems i.e., long range motion of the carriers.

Figure 5 illustrates the dielectric constant measured as a function of temperature (100–300 K) at 500 kHz. It is observed that dielectric constant increases with increase in temperature. The observed behavior of the dielectric constant with temperature can be explained as follows: at low temperature the ions can not orient themselves with respect to the direction of the applied filed, therefore, they posses a week contribution to the polarization and hence to the dielectric constant. As the temperature increases, the

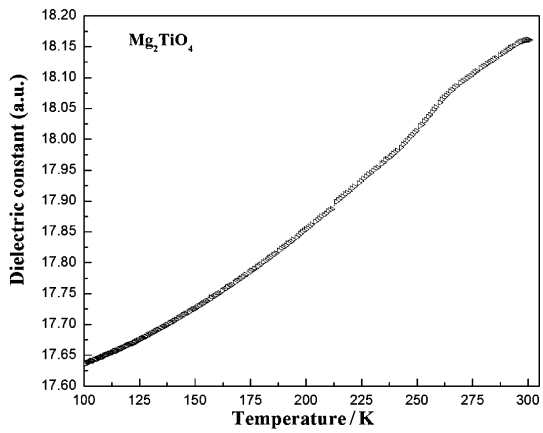


Fig. 5. Variation of dielectric constant as a function of temperature for Mg_2TiO_4.

conduction relies on the formation of the lattice defects under the action of thermal excitation, thus creating the vacancies through which ions motion may proceed under the action of external electric field. Therefore, with the increase in the temperature the ions get enough thermal energy to be able to obey the change in

the external field more easily. This in turns enhance their contribution to the polarization leading to an increase in the dielectric constant of the material. The value of the loss tangent was found to be very small ~0.01 and is constant throughout the whole temperature range.

4. Conclusion

In summary, we have successfully synthesized Mg_2TiO_4 by double sintering solid state reaction technique. XRD spectra clearly indicated polycrystalline cubic spinel structure of the system. Raman spectroscopic study also confirms the formation of single phase Mg_2TiO_4. A relaxation peak at 9 MHz has been observed in the dielectric constant measured as a function of frequency. Small variation in the dielectric constant measured in the temperature range 100–300 K at 500 kHz reflects the poor conductivity of the material. The low value of the loss tangent ($\tan\delta$) or high quality factor (Q) clearly indicates that this material is good for technological applications. The value of the exponent (s) evaluated using the power found to be ~1, which indicates the strong correlation of carries in the system.

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