

DIELECTRIC PROPERTIES OF PbWO₄, PbMgWO₄ AND PbCaWO₄ COMPOUNDS

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ABSTRACT

PbWO₄, PbMgWO₄ and PbCaWO₄ have been synthesised by the solid solution route technique. XRD patterns show them to be tetragonal. Dielectric constant (K') and Dielectric loss (K'') of PbWO₄, PbMgWO₄ and PbCaWO₄ have been measured at 1 kHz in the temperature range of 300 K to 1050 K. The log K' vs T as well as log K'' vs T plot of PbWO₄, PbMgWO₄ and PbCaWO₄ shows rapid increase of dielectric constant above 640 K, 700 K and 650 K respectively.

KEYWORDS : Dielectric constant, Dielectric Loss, PbWO₄, PbMgWO₄, PbCaWO₄

Recently the optical and electrical properties of Scheelite structure have received much attention. PbWO₄, PbMgWO₄ and PbCaWO₄ belong to Scheelite structure with tetragonal unit cell. PbWO₄ was extensively studied during the last century. The luminiscence properties, electrical conductivity, dielectric constant and defect chemistry have been studied in the past years (Belsky et al., 1997; Wohlfroth, 1982; Maryini et al. 1999 and Zahan et al. 1998). Dielectric studies are informative in the study of ferroelectricity and phase transition (Srivastava, 1998). Besides electrical transport properties of 3d compounds are in general interesting from various point of view. This paper reports dielectric constant and dielectric loss of PbWO₄, PbMgWO₄ and PbCaWO₄.

MATERIAL PREPARATION AND EXPERIMENTAL PROCEDURE

The starting materials for the preparation of these compounds were PbO, MgO, CaO and WO₃ (of 99.99% purity, procured from Alfa Aesar, A Johnson Matthey Chemicals India Pvt. Ltd.). The stoichiometric amount of these oxides were mixed and heated in silica crucible for 50 h. at a temperature of 1140 K followed by one intermediate grinding and final product was cooled down slowly. The prepared compounds undergo the following solid state reactions.

The weight loss corresponding to oxygen on the right hand side of the reactions were observed in both cases.

To get confirmation regarding the complete formation of the prepared compounds, X-ray diffraction pattern of the sample was taken at room temperature using CuKα line (λ = 0.15418 nm) as shown in Figure 1-3. From

XRD pattern the values of d_{hkl} have been obtained using relation

$$d_{hkl} = \frac{0.15418 \times 10^{-9}}{2 \sin \theta} \quad (1)$$

From d_{hkl} values, structures of the studied compounds were resolved using usual procedure. All the peaks have been assigned with proper hkl values. The sharpness and the single reflection peaks of the XRD pattern of powder support the formation of single phase compound and no unreacted part of the starting material were left. The unit cell parameters are given in Table 1. The lattice parameters were used to calculate the theoretical density of the material..

The prepared compounds were pressed at pressure of 8.22 × 10⁻⁸ Nm⁻² to form pellets of circular cross section (Area ~ 0.9 × 10⁻⁴ m² and thickness ~ 0.3 × 10⁻² m). The pellets were then sintered in air for 28 hr at 1000K. The sintered pellets were polished with fine emery paper to make both the surfaces flat and parallel. Air drying conducting silver paint was applied to both faces of the sample for better electrical contacts. The mounting of pellet was done between the rigid silver electrode of sample holder.

The dielectric constant and dielectric loss were obtained by measuring the capacitance (C) and quality factor (Q) of the sample at different temperature and at frequency of 1kHz, using LCR-Q meter model 928,

$$K = \frac{Cb}{8.854 \times 10^{-12} A} \quad (2)$$

$$K = \frac{1}{RC_0} \quad (3)$$

Where b = the thickness, A = face area of the pellet, ω = frequency in Hz, R = resistance in Ω and C₀ = the capacitance of the empty capacitor in F respectively.

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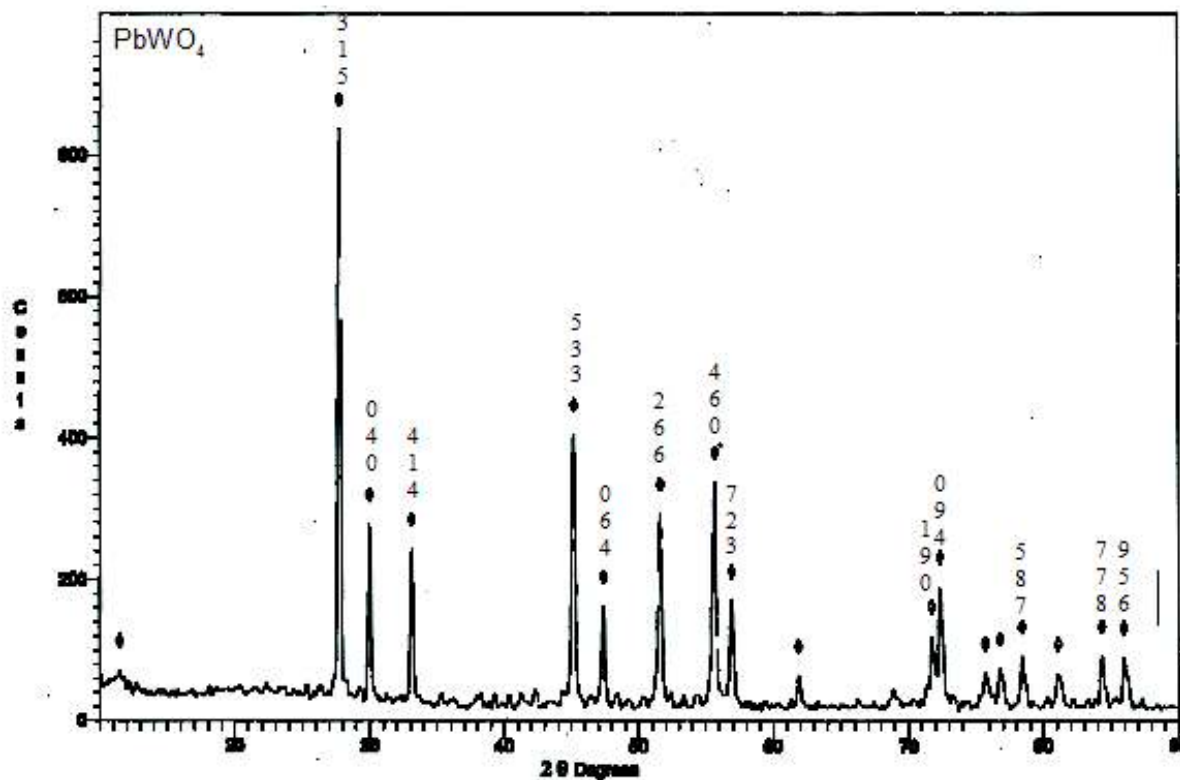


Figure 1 : X-ray diffraction pattern of PbWO_4

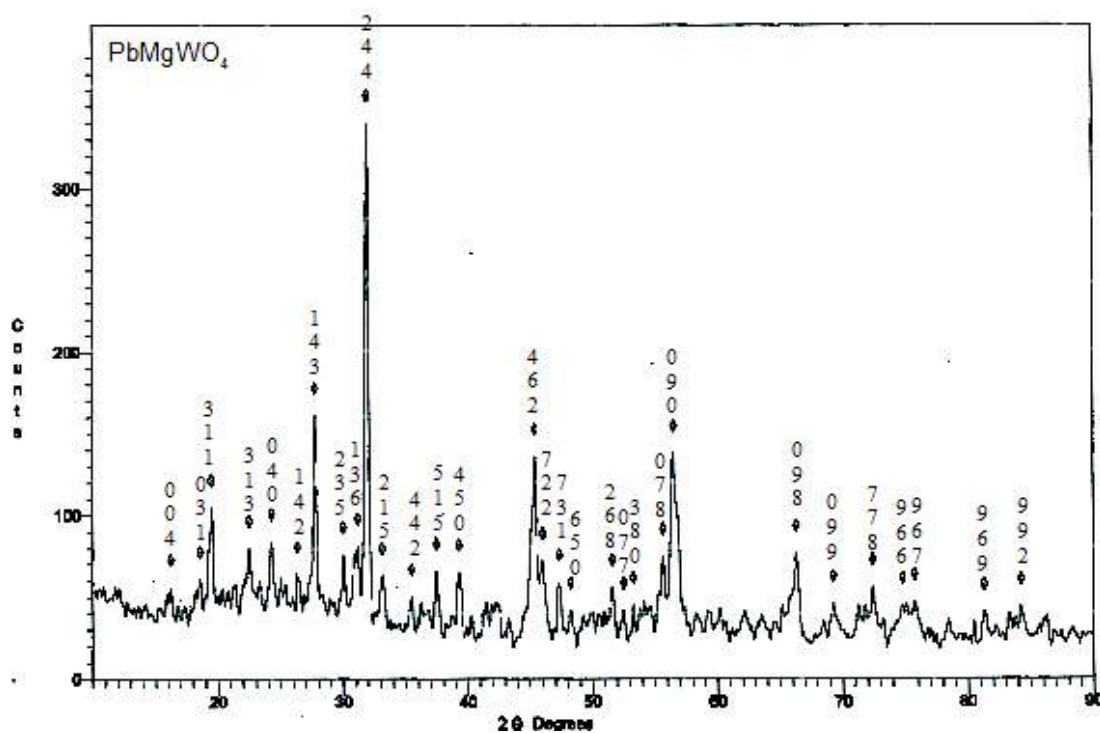
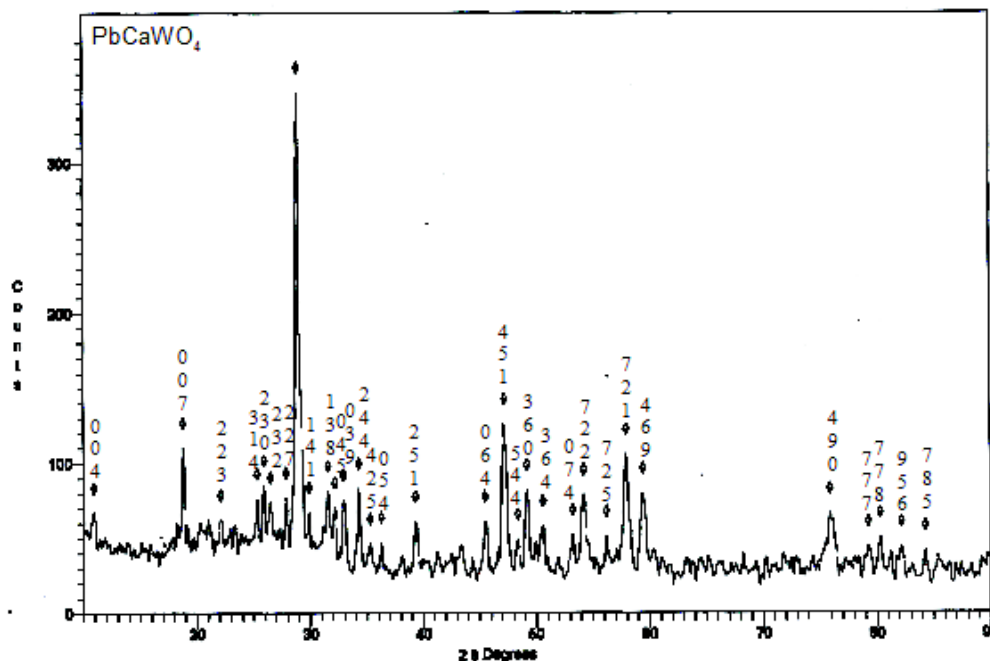


Figure 2 : X-ray diffraction pattern of PbMgWO_4

Figure 3 : X-ray diffraction pattern of PbCaWO₄

Systronics India. The measurements have been done in both heating and cooling cycles, but no significance differences have been observed. The dielectric constant (K') and dielectric loss (K'') of the material have been determined by using the following relations.

relation [10].

$$K'_b = \frac{\left(K'^{\frac{1}{3}} - P\right)^3}{1 - P} \quad (5)$$

The evaluated values of are given in Table-2.

RESULTS AND DISCUSSION

The variation of the dielectric constant (K') and dielectric loss (K'') with temperature at 1kHz is shown in Figure 4-6. It is seen from these plots that these compounds have high dielectric

constant from 40 to 58 at 400 K. Since dielectric constant (K') seems to have almost no temperature dependence, so these values may be taken as the room temperature values of the materials. The reported values of K' has been calculated using the capacitance value for the pressed pellets. The density of these pellets remains less than the theoretical density of these materials as given in Table-1. This means pellets contain air pores. Therefore a correction for pore fraction is essential to obtain the bulk value of the dielectric constant and is given by

$$f = \frac{d_0 - d_p}{d_0} \quad (4)$$

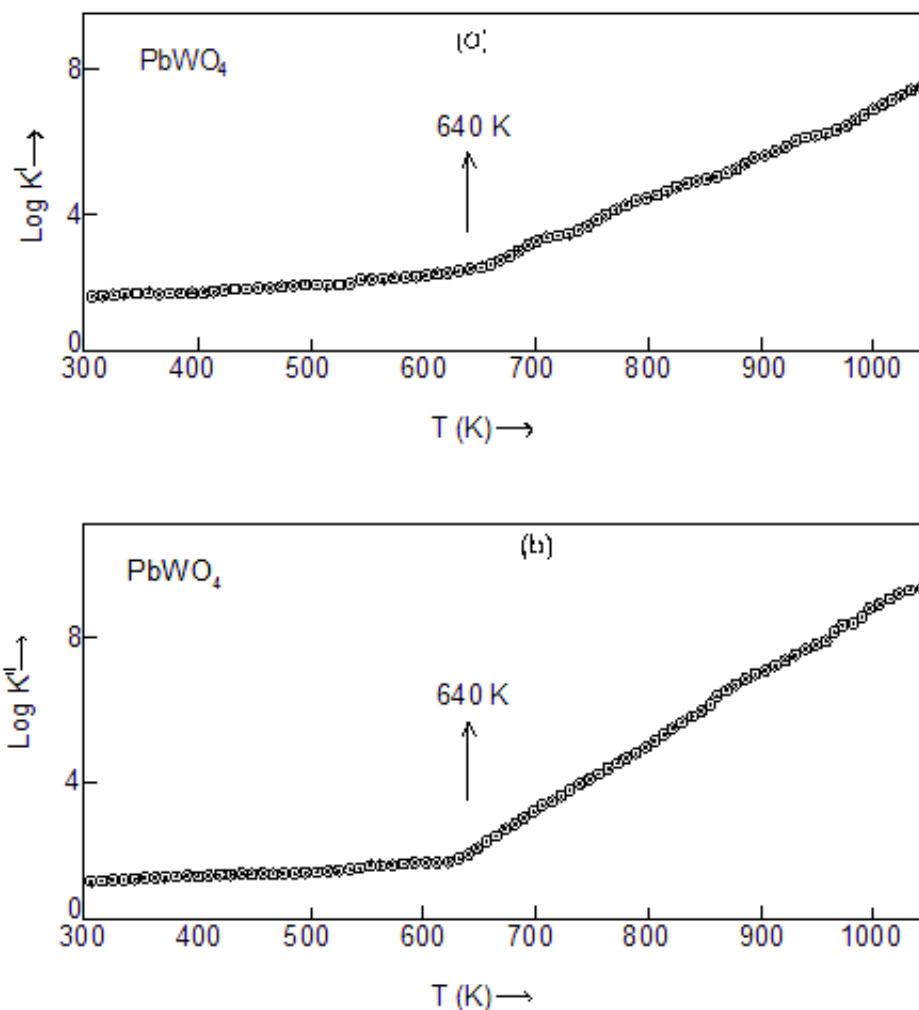
For low conducting solids, K' and P are related by the

Table 2 : The bulk value of dielectric constant of the studied compounds.

Compounds at 400 K	at 400 K
PbWO ₄	60
PbMgWO ₄	41
PbCaWO ₄	41

The values of K' of all these materials become large as temperature is increased and validity of equation (5) becomes doubtful. Further this formula change only magnitude of but not the nature of temperature variation of K' , therefore we have not used this correction at higher temperature.

The value of dielectric constant (K') and dielectric loss (K'') of all the studied materials at temperature 400 K, 600 K, 800 K and 1000 K at frequency 1 kHz are given in Table, 3 and Table, 4 respectively.

Figure 4 :Plots of dielectric constant ($\log K'$) and loss ($\log K''$) against absolute temperature (T) for PbWO_4 Table 3 : Dielectric constant (K') for studied tungstates at different temperature

Compounds	Dielectric constant			
	400 K	600 K	800 K	1000 K
PbWO_4	58	174	3.02×10^4	1.10×10^7
PbMgWO_4	40	58	5.24×10^2	6.31×10^4
PbCaWO_4	40	58	4.73×10^3	4.79×10^7

Table 4 : Dielectric loss (K'') for studied tungstates at different temperature

Compounds	Dielectric constant			
	400 K	600 K	800 K	1000 K
PbWO_4	19	40	9.12×10^4	9.12×10^8
PbMgWO_4	3	6	5.25×10^2	8.32×10^5
PbCaWO_4	4	9	3.02×10^4	3.98×10^9

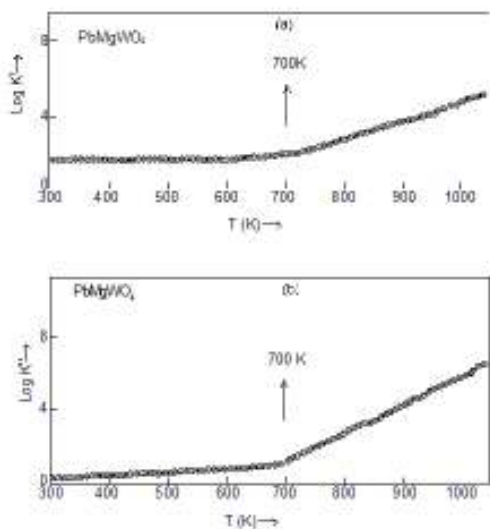


Figure 5 : Plots of dielectric constant ($\log K'$) and loss ($\log K''$) against absolute temperature (T) for PbMgWO_4

Table 5 : Break temperature obtained from dielectric constant and loss of studied tungstate

Break Temperature	Compound		
	PbWO_4	PbMgWO_4	PbCaWO_4
Tk	640	700	650

It is seen from the table that PbWO_4 has highest dielectric constant at 400 K. The dielectric constant has a very slow increase with temperature upto 600 K. The systematic trend of K' variation reveals that polarization mechanism in all these tungstates are same. A relatively larger value of K' in case of PbWO_4 appears due to the presence of chemical impurities which forms some kind of donor centres and have larger polarizability. The dielectric constant has very slow increase at lower temperature. This shows that there is no chance for the existence of thermally generated charge carriers at lower side of temperature. The lower value of K'' below 600 K indicates that free charge carriers generated from impurities is also small. The slow increase of K'' for all indicate that the thermally generated charge carriers below 600 K are small. This rules out the

possibility of strong space charge polarizability. Well made electrode rules out the chance of interfacial polarization. Therefore this slow increase seems to be the combined effect of lattice and electronic polarizabilities of individual ions. The increase of these polarizabilities seems to compensate the slight decrease of polarizability due to decrease in the number of ions per unit volume following the lattice expansion with temperature. However, it must be noticed that the increase of K' with T is very slow in comparison to the variation one expects for ionic solids. This indicates that either thermal expansion of these material is very small or they have some other kind of polarization mechanism.

It is seen from figures that dielectric constant (K') of all these materials have much faster increase at higher temperature. The dielectric loss (K'') also shows a rapid increase above certain critical temperature. It appears that higher increase in K' at higher temperature is due to space-charge polarization of thermally generated charge carriers. The break temperatures observed in K' and K'' are given in Table-5.

CONCLUSION

The dielectric constant (K') and loss (K'') have very slow increase upto temperature. However above, this increase becomes much more faster. The value of is different for different tungstates. The highest value of K' (~174) occurs for PbWO_4 upto temperature 600 K. The reason for faster increase of K' and K'' at higher temperature is due to space charge effect of thermally generated charge carriers.

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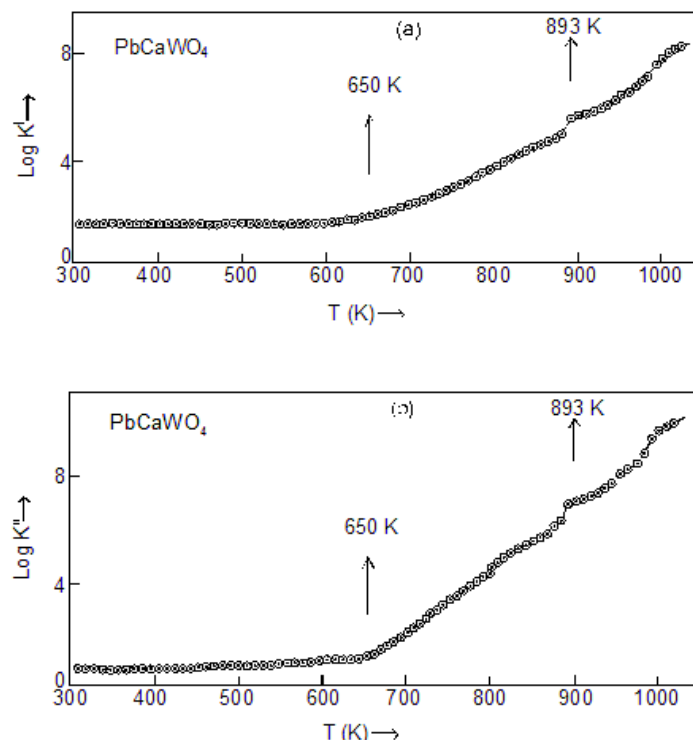


Figure 6: Plots of dielectric constant ($\log K'$) and loss ($\log K''$) against absolute temperature (T) for PbCaWO_4

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