Short Communication

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The Head Capacity, Cv, for Co^{2+}/MgO Single Crystal

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The heat capacity C_v for Co^{2+}/MgO single crystal as a function of temperature has been evaluated from the elastic constants data. These values agree well with those obtained from the calorimeter measurement. From the heat capacity data the entropy at 300K is estimated to be 20.86 $J\text{-}mol^{-1}\text{-}K^{-1}$.

Advanced systems for energy conversion, such as the magnetohydrodynamic generator, are generally designed to be operated at high temperatures. A serious obstacle to long-term performance of these systems is the degradation of the material used for electrical insulation [1]. Refractory insulators must be available which can withstand high-temperature operation without material degradation, such as electrothermal breakdown. It is therefore, important to recognize the parameters associated with the degradation - especially those which can improve the long-term characteristics. The impurity content is a parameter which has been known to shorten the characteristic times for breakdown [2- 3]. MgO is a refractory material of high chemical stability. It has been reported by Tsang and Chen [4] that the presence of Cu, Co, or H in MgO crystal suppresses the electrothermal breakdown and prolongs the lifetime of MgO crystal. In the case of crystals doped with 2000 ppm Co, the characteristic time for breakdown is 10 times longer than that of undoped (pure) crystals [4]. Heat capacity at constant pressure of single crystal MgO (pure) has measured from 300°k to 1200°k [5] and down to 20°k [6] by using calorimeter method. To observe the presence of impurities on the heat capacity, it has been decided to estimate the specific heat capacity C_v (at constant volume) for cobalt doped MgO single crystal, from the reported elastic constant data given by M.D. Hossain [7] which are measured from the Ultrasonic pluse-Echo Technique. Apart from this, the purpose of the present work is to evaluate the internal energy as well as entropy of MgO single crystals. No previous results on Co^{2+}/MgO in this regard have seemingly been published.

Specific beat capacity Cv (working formula). In 1912, Debye [8] realized that it is possible to propagate elastic waves through solids covering a wavelength region extending from low frequencies (sound waves) upto short waves (infrared absorption). According to him, the specific heat capacity, C_v, is given by the following expression:

$$C_V = 9NK_BZ\,(T/\theta_D)^3 \int_0^{\theta_D/T} \frac{x^4\, e^x}{(e^x - 1)}\, dx \qquad \text{.....(1)}$$

where θ_D, is known as a Debye characteristic temperature, N is the Avogadro number, K_B is the Boltzmann constant, T is the absolute temperature and Z is the number of atoms in one molecule. The temperature θ_D is an important parameter of a solid. It is found in equations describing properties which arise from atomic vibrations and in theories involving phonons.

Recently, the author has reported [7] the experimental results of the elastic constant of Co^{2+}/MgO (9900 ppm) by ultrasonic pulse echo-overlap technique at room temperature. The values of these constants are as $C_{11} = 28.50x^{11}$ dynes/cm^2, $C_{12} = 8.61x10^{11}$ dynes/cm^2 and $C_{44} = 15.21x10^{11}$ dynes/cm^2. One of the standard methods of calculating the Debye temperature θ_D is from the elastic constant data, since θ_D is proportional to the sound velocity (averaged) $\bar{V}_m$. The relation between θ_D and $\bar{V}_m$ is shown in section III, and $\bar{V}_m$ with the elastic constants is shown in section IV.

Relation between debye temperature θ_D and averaged sound velocity $\bar{V}_m$. It has been shown by Huntington [9] that the Debye temperature, θ_D, is proportional to the mean sound velocity, $\bar{V}_m$ of a solid in the form

$$\theta_D = \frac{h}{K_B}\left\langle\frac{3ZN\rho}{4\pi M}\right\rangle^{1/3} V_m \qquad \text{.....(2)}$$

where h is Planck's constant, N is Avogadro number, M is the molecular weight of the solid, and ρ is the density. {For Co^{2+}/MgO, Z = 2, ρ = 3.61 gm per cm^3 [7]}.

The use of Equation -2 is often hindered by the problem of computing V_m. Since θ_D is scalar, it follows that V_m must also be a scalar, and herein lies the difficulty of this equation. The stress is a tensor quantity and for each direction in a crystal, there are three velocities each of which is a complicated function of the stress components. The expression for V_m is given by Huntington [9] is

$$\bar{V}_m\left[\frac{1}{3}\sum_{i=1}^{3}\int_0^{4\pi}\frac{1}{V_i^3}\frac{d\Omega}{4\pi}\right]^{-1/3} \qquad \text{.....(3)}$$

Equation -3 can be solved for a solid only by a rigorous computation based on the precise knowledge of the elastic

constants of the crystal. Anderson [10], however, showed that Equation -3 can be substituted by the following simple equation to determine the mean sound volocity for all solids.

$$\bar{V}_m \left[\frac{1}{3} \left\langle \frac{1}{\bar{V}_s^3} + \frac{1}{\bar{V}_l^3} \right\rangle \right]^{-1/3} \quad \text{.....(4)}$$

where V_s and V_l are the mean shear and longitudinal sound velocities respectively. According to Gilvarry [11] the parameters V_s and V_l can be defined by the following formula.

$$\bar{V}_S = \left[\frac{G_H}{\rho} \right]^{1/2} \quad \text{.....(5)}$$

$$\bar{V}_L \left[\frac{\langle K_H + \frac{3}{4} G_H \rangle}{\rho} \right]^{1/2} \quad \text{.....(6)}$$

where the symbols G_H and K_H represent bulk modulus and shear modulus for the cubic single crystal. The temperature dependence heat capacity C_v is then calculated by using equation 1 and 2.

Specimen history: The doped single crystal of Co^{2+}/MgO was obtained from W&C Spicer Ltd. (U.K.) having been grown by electrofusion using pure powdered cobalt oxide and pure powder magnesia as starting materials. The cobalt concentration in the specimen was 9900 ppm, this had been determined by X-ray fluorescent analysis (Johnson and Mathey Ltd.). The crystalline quality was good and neither optical examination nor X-ray back reflection photograph, used to orient the specimens, revealed any evidence of macroscopic cracking, flaws, strain or mosaic formation. The colour of the crystal was deep pink. ESR measurements on this specimen [12] showed only line due to Co^{2+} which suggests that the crystal has got no other impurities. This is due to the fact that, since Co^{2+} ion is doubly charged, a direct substitution for Mg^{2+} is possible in the MgO lattice without the need for charge compensating vacancies.

Ultrasonic pulse-echo overlap technique. The elastic constants of Co^{2+}/MgO were determined from the ultrasonic velocity measurements by pulse echo-overlap method. Ultrasonic wave pulses were generated and received with X-cut (for longitudinal waves) and Y- cut (for shear waves) quartz transducers of 6 mm diameter with a resonance frequency of 15 mHz as described by M.D. Hossain [7]. In this system the R.F. Unit, which delivers pulses to the sample and the resultant unrectified echo train is displayed on the oscilloscope. The RF generator is riggered by the frequency synthesiser output divided by one hundred or one thousand, so that any given echo train has completely decayed before the next RF pulse. The technique now is to overlap two of the echoes by triggering from the frequency synthesiser. When the set frequency is an exact multiple of the inverse transit time, the echoes overlap each other precisely. In this situation all the RF oscillations are in phase and the maxima of each echo coincident. The transit time for the RF pulse within the specimen is now the reciprocal the trigger frequency. The distance between each successive peak on each train represents twice the transit time of the ultrasound pulse across the sample. Therefore once the sample length has been measured, the ultrasound velocity can be obtained as the distance travelled divided by the transit time.

By using the experimental values of elastic constants of Co^{2+}/MgO [7], the temperature dependence of heat capacity C_v in the temperature range up to 1200K, have been evaluated with the help of the equations given in the Section II and III. The calculated values of C_v for Co^{2+}/MgO are plotted in Fig. 1(a) by dotted line. The reported values of C_v for pure MgO single crystal shown in Fig. 1(b) by solid line, which are obtained from the measured values of C_p from the calorimeter method [5,6]. Comparison between the calculated results for the Co^{2+}/MgO single crystal and those reported from calorimeter method for MgO single crystal shows that both the results are very close to each other. This supports the validity of the present method of calculation of C_v from the elastic constant data. Though it has been shown in the literature [4] that the certain impurities do indeed enhance the electrical breakdown in MgO crystals, but on the other hand the present study shows that the heat capacity, C_v of MgO crystal is independent of divalent cobalt doped concentration.

The internal energy U, has been calculated by using the following equation:

$$U = 9 N K_B T (T/\theta_D)^3 \int_0^{\theta_D/T} \frac{x^3}{e^x - 1} dx \quad \text{.....(7)}$$

and the calculated values are shown in Fig. 1(c). These values are useful for the evaluation of free energy.

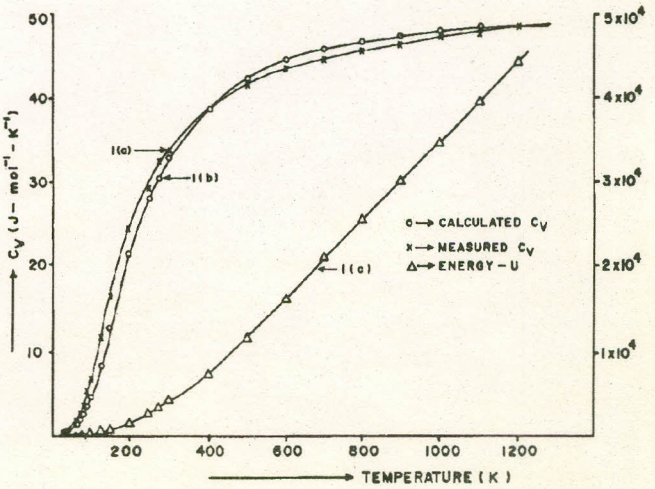

Fig. 1. Energy and heat capacity, C_v (for Co^{2+}/ MgO) with temperature.

The entropy S, at 300K is obtained from the relation,

$$S = \int_0^{300} \frac{C_V}{T}\, dT \quad \text{.....(8)}$$

$$= 20.86 \text{ J-mol}^{-1} \text{–K}^{-1}$$

This is comparable to the literature value S=26.91 $J.mol^{-1}$ K^{-1} of MgO at 300K [6] and thus again supports the validity of the present method of evaluation of C_v.

In conclusion, it can be said that the present study of heat capacity and internal energy as a function of temperature reveals additional information about the thermal properties of Co^{2+}/MgO single crystal and this knowledge may be helpful for understanding the various problems of conduction mechanism for materials of structure like MgO.

Key words: Heatcapacity, Debye temperature, MgO single crystal.

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