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Research Article

Thermal Conductivity of Gel-Grown Barium Oxalate at 326 and 335 K

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Single crystals of barium oxalate have been grown by gel method using agar-agar gel as media of growth at ambient temperature. The grown crystal crystallizes under monoclinic structure. Thermal conductivity of gel-grown barium oxalate crystals as a function of temperature has been studied at 326 and 335 K by using divided bar method. The thermal conductivity of barium oxalate crystal at 326 K was found 3.685 W m^{-1} K^{-1} and 3.133 W m^{-1} K^{-1} at 335 K. The reduction of thermal conductivity with the rise in temperature may be due to reduction in mean free path of phonons in the solid.

1. Introduction

A material possessing both very high and very low thermal conductivities has a wide range of applications. Solid materials like diamond and silicon have high thermal conductivity, and therefore they are used in thermal electronic devices [1–8]. Low thermal conductivity materials like skutterudites [9, 10], clathrates [11, 12], and Zintl phases [13] have high thermoelectric efficiency [14]. The thermal conduction in solid is directly correlated with the harmonicity and anharmonicity of thermal vibrations. Thus, materials possessing harmonic thermal vibrations are responsible for very high thermal conductivity, whereas anharmonic vibrations are attributed for low thermal conductivity. A number of factors like impurities, dislocations, and crystal boundaries contribute to thermal conduction in solids.

Well facet prismatic, platy-shaped, transparent crystals were grown by gel method using agar-agar gel as media of growth at ambient temperature [15, 16].

Since barium oxalate is a pyronature material, which shows great promise in pyrotechnic and high temperature electronic applications [17, 18], it is therefore interesting to investigate the thermal properties such as thermal conductivity of this material.

The quantity of heat that passes through a substance in unit time of unit area and unit thickness, when its opposite faces differ in temperature by one degree, is known as thermal conductivity. The SI unit of thermal conductivity κ is Watt per meter Kelvin ($W\,m^{-1}\,K^{-1}$). Measurement of thermal conductivity is an important property for investigating lattice defects or imperfection in solid. This property also provides an opportunity for investigating existing intriguing physical phenomenon, and therefore to study thermal conductivity of solid material is of great technological interest.

In the present work, thermal conductivity of crystals as a function of temperature has been studied at 326 and 335 K.

2. Experimental Procedure

The growth of barium oxalate was carried out in agar-agar gel. U-tube and a single glass tube were used as crystallizing vessels. Agar-agar gel was prepared by dissolving agar-agar powder in double-distilled water at boiling temperature.

In double diffusion, the U-tube was filled up to proper heights with hot agar-agar solution and was kept for setting. After setting and aging gel, a solution of oxalic acid was poured in one limb and a solution of barium chloride was poured in the other limb of the U-tube. Nucleation was observed inside the gel after one week. This nucleation was further increased and led to dendrite growth after ten to twenty days. As the reactants solution diffuses deep into

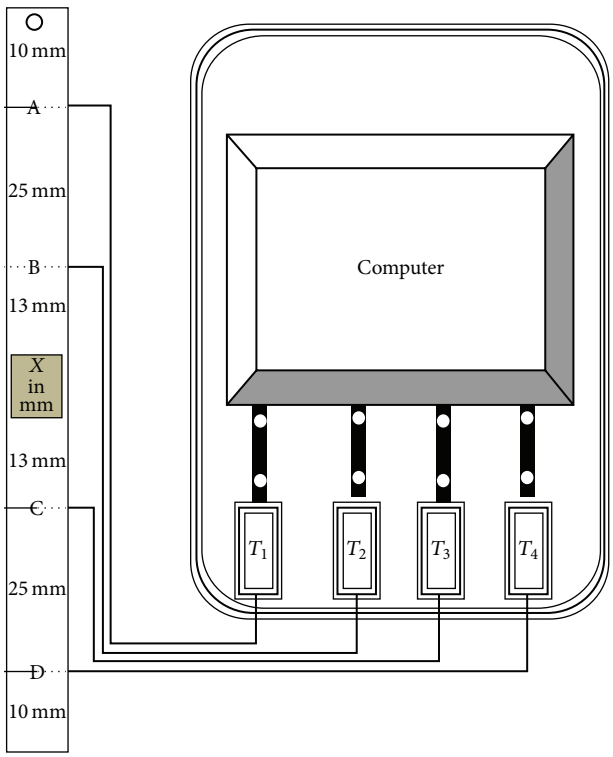

Figure 1: A schematic presentation of equipment for measurement of thermal conductivity.

the gel, prismatic, platy-shaped, transparent crystals were found to grow at the interstitial.

In single diffusion, hot aqueous agar-agar gel and a solution of barium chloride were mixed and kept in test tube for setting. After setting and aging the gel, a solution of oxalic acid was added above the gel. Nucleation was observed within a day just below the interface. This nucleation were further led to dendrite growth. After two to three days, many single nuclei were observed below the dendrite growth at the middle and also at the lower end of test the tube. These nuclei have grown to prismatic, platy-shaped, transparent crystals.

The powder XRD pattern of grown crystals was obtained using a Miniflex, Rigaku X-ray diffractometer with CuKα radiation.

Thermal conductivity of grown barium oxalate single crystals was measured at 326 and 335 K on a well-equipped instrument assembled by the Department of Physics, Sardar Patel University, Vallabh Vidyanagar (Gujarat), and its schematic diagram is shown in Figure 1.

The equipment is interfaced with, computer to record directly the temperatures of sectional parts of metal rod with the help of thermocouple junctions; a crystal 2.1 mm thick was fixed in a stainless steel bar at a position X. Four thermocouple sensors were fitted in a measured distance at positions A, B, C, and D. By using electrical heating plate, one end "O" of metal bar was heated and kept at constant temperature 326 K throughout the experiment. Temperatures of a metal bar at thermocouple positions A, B, C, and D were measured every minute and recorded on a computerized

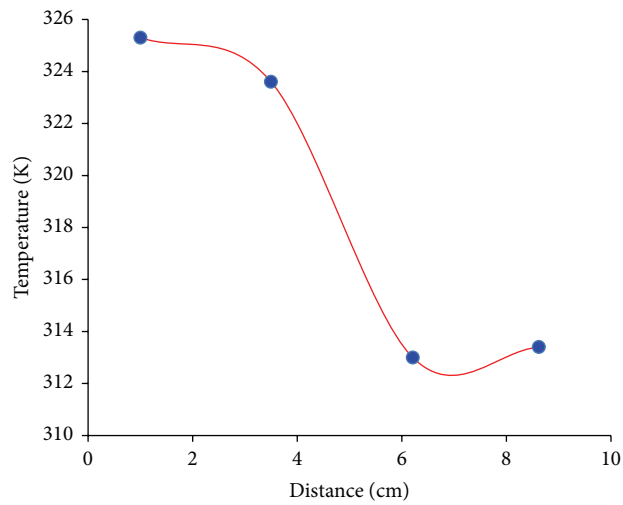

Figure 2: Plot of temperature versus distance on a rod at different positions for barium oxalate at 326 K.

system. Successive lowering of temperature with increasing distance from heating end "O" of metal rod at A, B, C, and D was observed, and the average temperatures at each of the positions were simply determined. A plot of temperature versus distance on a rod at positions A, B, C, and D is shown in Figure 2.

An exactly similar experiment was also carried out using another barium oxalate crystal of 1.5 mm thickness, and the temperature was measured at the same positions by keeping the temperature constant at one end of a metal rod at 335 K. A plot of temperature versus distance at positions A, B, C, and D is shown in Figure 3. From these graphs the temperature gradients and thereby coefficient of thermal conductivity, κ_c, of the crystal were calculated using the equation

$$\kappa_c = \kappa_m \left[\frac{(dT/dx)_m}{(dT/dx)_c} \right], \tag{1}$$

where κ_m is the coefficient of thermal conductivity of the metal, $(dT/dx)_m$ is the temperature gradient of metal, and $(dT/dx)_c$ is the temperature gradient of the crystal.

3. Observations and Results

From the X-ray diffractogram of barium oxalate [15], d values for different h, k, l were computed. The computer program POWD (an Interactive Powder Diffraction Data Interpretation and Indexing Program, Version 2.2) was used to calculate "d" values, lattice parameters, and the system of the grown crystals.

To measure thermal conductivity of barium oxalate crystals, temperatures were recorded every minute at A, B, C, and D, keeping one end "O" at 326 K and 335 K, respectively.

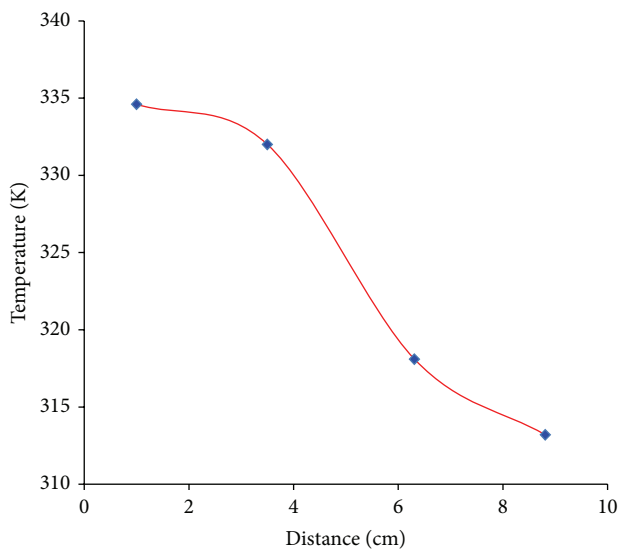

Figure 3: Plot of temperature versus distance on a rod at different positions for barium oxalate at 335 K.

3.1. Determination of Thermal Conductivity of Crystals (κ_c)

3.1.1. Thermal Conductivity of Crystal at 326 K. Thermal conductivity of stainless steel metal bar (std. value) is

$$\kappa_m = 3.8 \times 10^{-2}\ \text{cal sec}^{-1}\ \text{cm}^{-1}\ \text{degree}^{-1}. \tag{2}$$

Temperature gradient from Figure 2 is

$$\left(\frac{dT}{dx}\right)_m = 0.6728, \qquad \left(\frac{dT}{dx}\right)_c = 2.905. \tag{3}$$

On substituting these values in the equation

$$\kappa_c = \kappa_m \left[\frac{(dT/dx)_m}{(dT/dx)_c}\right]$$
$$\therefore (\kappa_c)_{326\,\text{K}} = 0.008801\ \text{cal sec}^{-1}\ \text{cm}^{-1}\ \text{deg}^{-1}. \tag{4}$$
$$\text{That is, } (\kappa_c)_{326\,\text{K}} = 3.685\ \text{W m}^{-1}\ \text{k}^{-1}.$$

3.1.2. Thermal Conductivity of Crystal at 335 K. Similarly, using temperature gradient from Figure 3, the value of κ_c at 335 K will be

$$(\kappa_c)_{335\,\text{K}} = 0.007483\ \text{cal sec}^{-1}\ \text{cm}^{-1}\ \text{deg}^{-1}.$$
$$\text{That is, } (\kappa_c)_{335\,\text{K}} = 3.133\ \text{W m}^{-1}\ \text{k}^{-1}. \tag{5}$$

4. Discussion

The compound crystallizes under monoclinic structure as reported [15].

The thermal conductivity equation implies that the process of thermal energy transfer is a random process. The energy does not simply enter one end of the specimen and proceed directly in a straight path to the other end, but rather the energy diffuses through the specimen, suffering frequent collisions; such conductivity process brings the temperature gradient.

Resistance to heat flow in dielectric solids arises from scattering of phonons by defects in the crystal structure such as lattice defects, grain boundaries and presence of isotopes and impurities. The thermal conductivity of nonmetallic crystal solid is due to phonon interaction. The collisions of phonons with each other result in an alteration of phonon frequencies and their moments. In the harmonic solid, such phonon-phonon interactions are not possible; thereby, such solid possesses high thermal conductivity. In solids with anharmonic lattice interactions, there is a coupling between different phonons, which limits the value of the mean free path and hence lowers the thermal conductivity [19, 20].

As mentioned previously a perfect harmonic crystal has no thermal resistance mechanism; hence it has infinite thermal conductivity. This point was addressed by Slack [19] from the perspective of insulators in which the phonons are maximally coupled and as a function of the number of atoms in the unit cell. The thermal conductivity of some crystalline solid approaches minimum as the temperature reaches melting point [19].

The thermal conductivity of barium oxalate crystal at 326 K was found to be 3.685 and 3.133 W m^{-1} K^{-1} at 335 K. The reduction of thermal conductivity with the rise in temperature may be due to reduction in mean free path of phonons in the solid. These experimental results in the present work are well in agreement with the Slack findings [19]. The concept of minimal thermal conductivity can be a useful guide and attempt to develop material with exceptionally low thermal conductivities, for example, thermoelectrics. The thermal conductivity of an insulator can be reduced either by increasing the size of the unit cell, the pressure of heavy atoms, random atomic substitution, increasing optic acoustic couplings, or increasing lattice symmetry [19].

5. Conclusion

From systematic investigation and study of gel-grown barium oxalate crystals, the following pointwise conclusions were drawn.

(a) Gelgrown barium oxalate has a crystalline nature and crystallizes under monoclinic system.

(b) The thermal conductivity of barium oxalate crystal is decreasing with increasing the temperature which may be due to reduction in mean free path of phonons.

(c) Low thermal conductivity of this material can lead to developing it as a thermoelectric material.

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