

EFFECT OF THE CATION COMPOSITION OF CARBONATES ON THEIR THERMAL PROPERTIES

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A specific behavior of the heat conductivity and thermal diffusivity of isomorphous carbonates was studied experimentally under normal conditions. A new semiempirical formula was derived for the dependence of the heat conductivity of isomorphous minerals on a metallic ion mass-to-anion mass ratio. It was found that the heat conductivity and thermal diffusivity of carbonates decreased with the increasing of the values of their mean atomic weights (or metallic cation masses).

An important problem of research into a heat transfer mechanism in minerals is to study the effect of isovalent cation replacement on thermal properties of the matter. In our experiment we used minerals of a carbonate series. Carbonates belong to a group of major rock-forming minerals in the rocks of the upper lithosphere which is in direct contact with the hydrosphere and atmosphere and, hence, is undergoing a continuous evolution. The formation of carbonate-bearing rocks is related to the deposition and alteration of the products of living organism's activity. In this context the knowledge of the thermal properties of carbonate-bearing rocks and carbonate-group minerals is important not only for the study of the Earth's thermal field and fundamental problems of solid-state physics, but also can be useful for the solution of some ecologic problems.

We measured thermal properties of minerals using a set-up that had been designed and manufactured at the Faculty of Physics, Department of Physics, Moscow State University. This set-up is designed for multipurpose studies of the thermal properties of rocks. When used with a special measurement unit, this set-up allows one to run experiments with liquid and moisture-saturated materials [1] with a simultaneous measurement of thermal diffusivity, heat capacity, and thermal conductivity (α , C_p , λ) at room temperature and atmospheric pressure with a sufficiently high accuracy ($\Delta\alpha/\alpha \sim 3\%$, $\Delta C_p/C_p \sim 3\%$, $\Delta\lambda/\lambda \sim 7\%$).

The results of our experimental measurements of thermal diffusivity, thermal conductivity, and density of carbonate minerals are presented in Table 1.

Thermal diffusivity (thermal energy diffusion coefficient) is an important thermal characteristic of the matter, which is directly related to a heat-transfer mechanism. Thermal diffusivity of crystalline dielectrics, in which heat is transferred by way of lattice vibration, can be computed using the formula $\alpha = (1/3)\bar{V}\bar{l}$, where \bar{l} is the mean length of a phonon free path, and \bar{V} is the mean sound velocity. The process of heat transfer in a crystal is treated as a process of energy exchange between the phonons, and heat conductivity is assumed to have the form $\lambda = (1/3)C_v\bar{V}\bar{l} = C_v\alpha$, where C_v is the heat capacity of a unit volume. In the Debye-Peierls theory, \bar{V} is taken to be independent of temperature, and, hence, in the classical temperature range, where $C_v \cong \text{const}$, thermal conductivity is controlled by the mean length of a phonon free path alone, the parameter that can be calculated using data on thermal diffusivity. The knowledge of the \bar{l} value, in its turn, enables one to estimate the intensity of phonon-phonon interactions, namely, the processes of the throw-over and phonon scattering on structural defects, these phonons including heavy-metal cations in the

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Table 1
Thermal Properties of Carbonates under Study

Mineral	Formula	System	$\langle M \rangle$	ρ , kg/m ³	$a \times 10^7$, m ² /s	λ , W/(m·K)
Magnesite	MgCO ₃	Trigonal	16.86	2895	25.0	5.57
Dolomite	CaMg(CO ₃) ₂	Trigonal	18.44	2711	22.2	4.63
Calcite	CaCO ₃	Trigonal	20.02	2648	17.3	3.52
Siderite	FeCO ₃	Trigonal	23.17	3591	11.9	3.23
Aragonite	CaCO ₃	Orthogonal	20.02	2662	12.7	2.60

isostructural series of rock-forming minerals. However, data on systematic measurements of the thermal diffusivity of isomorphous minerals are scarce, and the results of our experiment may fill this gap as regards the carbonate series.

Variations of the thermal diffusivity and heat conductivity of our carbonates as a function of their mean atomic weights are presented in Figs. 1 and 2.

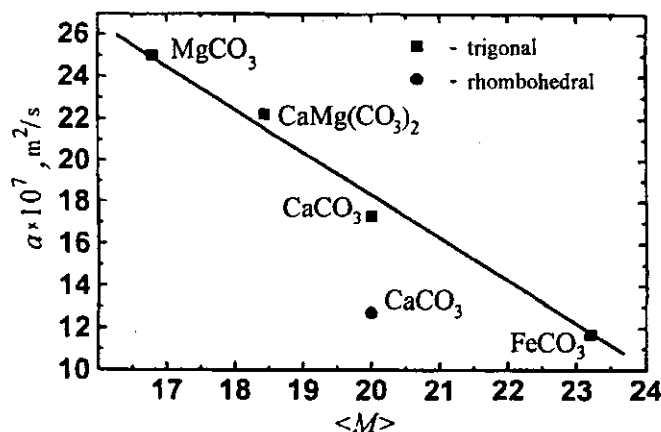


Fig. 1

Thermal diffusivity of the carbonates of a trigonal and a rhombohedral systems as a function of their mean atomic weights.

One can see that both of these parameters decrease with the increasing of mean atomic weights of the carbonate compounds, even though, in contrast to thermal diffusivity, heat conductivity shows a nonlinear variation.

In addition to our measurements, we plotted in Fig. 2 the data reported by K. Horai [2] who was the first to carry out a systematic study of heat conductivity of various isomorphous series of natural minerals, including carbonates of the trigonal system. He concluded that the thermal conductivity of minerals, members of the series of isovalent replacement, decreased linearly with the increasing of mean atomic weights. He explained this phenomenon by the fact that the efficiency of phonon scattering increased in isomorphous minerals during the isovalent replacement of light cations by heavier ones. In order to investigate this phenomenon in more detail, G. I. Petrunin and V. G. Popov [3], Faculty of the Earth's Physics, Moscow State University, examined a series of artificial garnets with known compositions and known distribution of defects. Their experiments showed that both the thermal diffusivity and heat conductivity of simple garnets decreased with the increasing of mass of a replaced cation. They observed an interesting phenomenon: the

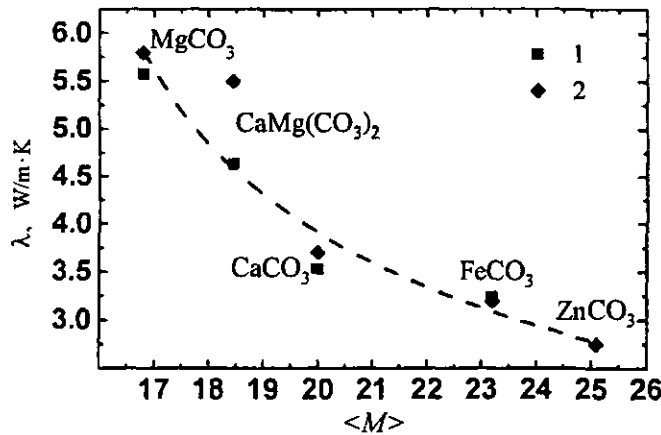


Fig. 2

Thermal conductivity of monomineral carbonates as a function of their mean atomic weights: (1) our data, (2) K. Horai's data [2].

mean phonon lifetime, calculated from thermal diffusivity and mean sound velocity values, was identical for all simple garnets with an accuracy of 1–2% ($\tau = 5.64 \times 10^{-13}$ s) [3]. This implies that the decline of diffusivity and thermal conductivity in their experiment was related to a decrease in the effective velocity of phonon propagation rather than to an increase in scattering intensity, as it was postulated by K. Horai.

The results of our experiment confirm that the mean length of a free phonon path decreases with the increasing of the mean atomic weight [2]. However, lack of sound velocity data prevented a more detailed analysis of this effect. As regards the nonlinear relationship between the thermal conductivity of carbonates and their mean atomic weights, we found it to be controlled mainly by the similar behavior of the volumetric heat capacity $C_v = C_p \rho$ and to be unrelated to the nonlinear variation of phonon lifetime or to phonon propagation velocity. Nevertheless, some influence of these factors cannot be ruled out, especially in terms of the great variation range of the mean atomic weights of the carbonates. For instance, the data reported in literature [4] on the heat conductivities of alkaline metal halides suggest that a relationship between the heat conductivities of materials with an isovalent replacement and their mean atomic weights may be nonlinear and have a peak where cation and anion masses are equal. For instance, A. S. Povarennykh and co-authors [4] reported the RbBr heat conductivity to be 4.0 W/(m·K), which is substantially higher than the value of 2.6 W/(m·K) for NaBr, even though the mean atomic weight of RbBr (82.67) is much higher than that of NaBr (51.45). This suggests a conclusion that is directly opposite to that of K. Horai. The higher thermal conductivity of RbBr can be explained in this case by the fact that a decrease in a difference between the oscillating masses that takes place as the ratio between the cation and anion masses approaches the value of 1 affects the growth of the average length of a free phonon path to a significantly higher extent than does the growth of an interatomic distance (a factor that lowers thermal conductivity).

The heat conductivities of other halides (e. g., chlorides) [5], whose cation masses are larger than their anion masses, suggest that as the mean atomic weight (KCl, RbCl, CsCl) increases, the heat resistance increases simultaneously with the growth of a cation/anion ratio.

In the light of these inferences, K. Horai's conclusion concerning the heat conductivity behavior with the increasing of the atomic weight of a carbonate compound becomes understandable. Among the carbonates he used in his experiments, magnesite (MgCO₃) had the lowest atomic weight, similar to our experiment. However, the atomic weight of magnesium (24.31) exceeds the mean atomic weight of the CO₃ group (15.0), not to mention the other carbonates. In other words, Horai's experiment was concerned with that segment of the thermal conductivity curve, where the decline of the latter was related to the growth of structural imperfection caused by the greater fluctuation of masses in the crystalline space. This suggests a new line of a more detailed research into the effect of a cation and anion mass difference upon the thermal properties of rock-forming minerals and other materials of a complex atomic composition.

To interpret the results of our experiments, we invite the reader to consider an oscillation of a connected system of two bodies with masses m_1 and m_2 (Fig. 3).

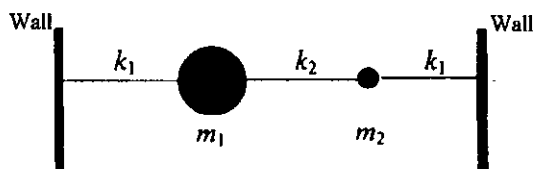


Fig. 3

System of two bodies with elastic bonds k_1 and k_2 and masses m_1 and m_2 .

The higher the temperature, the more short-wave phonons are in the system. In fact, this implies that a mean difference between the oscillation phases of the neighboring atoms grows with the increasing in temperature. If the frequency of atom oscillations is conformable with the wavelength equal to a double distance between the atoms, the latter oscillate in an opposite phase.

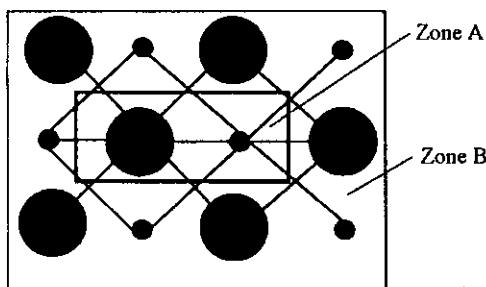


Fig. 4

Idealized distribution of atoms in a crystal.

The role of "walls" in the crystalline lattice is played by the neighboring atoms (Fig. 4). Here, Zone A is a region where energy is transferred from one atom to another; Zone B contains atoms that oscillate, relative to the ones concerned, with a greater phase shift and, hence, act as "holders" (walls). For simplicity, we take $k_1 = k_2 = k$, where k is a binding force coefficient. Using a linear approximation, we can describe the movements of this bound system by the following equations:

$$\begin{cases} m_1 \frac{d^2 x_1}{dt^2} = -k_1 x_1 + k_2 (x_2 - x_1), \\ m_2 \frac{d^2 x_2}{dt^2} = -k_1 x_2 - k_2 (x_2 - x_1) \end{cases}$$

or

$$\begin{cases} \frac{d^2 x_1}{dt^2} + \omega_{11}^2 x_1 - \omega_{12}^2 x_2 = 0, \\ \frac{d^2 x_2}{dt^2} + \omega_{22}^2 x_2 - \omega_{21}^2 x_1 = 0, \end{cases}$$

where $\omega_{11}^2 = (k_1 + k_2)/m_1 = 2k/m_1$, $\omega_{12}^2 = k_2/m_1 = k/m_1$, $\omega_{22}^2 = (k_1 + k_2)/m_2 = 2k/m_2$, and $\omega_{21}^2 = k_2/m_2 = k/m_2$.

Using the substitution $x_1 = A_1 e^{i\omega t}$ and $x_2 = A_2 e^{i\omega t}$, we find the natural frequencies of the oscillations and ratios between the coefficients for each frequency:

$$\omega_1^2 = \frac{k}{\mu} \left[1 + \frac{1}{1 + \eta} \xi \right], \quad A_{21} = A_{11} (1 - \eta - \xi), \quad (1)$$

$$\omega_2^2 = \frac{k}{\mu} \left[1 - \frac{1}{1+\eta} \xi \right], \quad A_{22} = A_{12}(1 - \eta + \xi), \quad (2)$$

where $\mu = m_1 m_2 / (m_1 + m_2)$ is a reduced mass, $\eta = m_1 / m_2$, and $\xi = \sqrt{1 - \eta + \eta^2}$.

We can now write a solution in the form

$$\begin{aligned} x_1 &= a_1 \sin(\omega_1 t + \varphi_1) + a_2 \sin(\omega_2 t + \varphi_2), \\ x_2 &= a_1(1 - \eta - \xi) \sin(\omega_1 t + \varphi_1) + a_2(1 - \eta + \xi) \sin(\omega_2 t + \varphi_2), \end{aligned}$$

where a_1 and a_2 are arbitrary constants.

Specifying the boundary conditions, we let $t = 0$, $x_1 = x_2 = 0$, $dx_1/dt = V$, and $dx_2/dt = 0$. Having found expressions for the coefficients and initial phases, we get

$$\begin{aligned} x_1 &= \frac{V}{\omega_1} \frac{1 - \eta + \xi}{2\xi} \sin(\omega_1 t) - \frac{V}{\omega_2} \frac{1 - \eta - \xi}{2\xi} \sin(\omega_2 t), \\ x_2 &= -\frac{V}{\omega_1} \frac{\eta}{2\xi} \sin(\omega_1 t) + \frac{V}{\omega_2} \frac{\eta}{2\xi} \sin(\omega_2 t). \end{aligned}$$

For the kinetic energy of a body with a mass m_2 , we have

$$\frac{1}{2} m_2 \left(\frac{dx_2}{dt} \right)^2 = \frac{m_2 V^2}{2} \frac{\eta^2}{\xi^2} \sin^2 \left(\frac{\omega_1 - \omega_2}{2} t \right) \sin^2 \left(\frac{\omega_1 + \omega_2}{2} t \right).$$

Such oscillations are known to have a mode of beatings. The amplitude of the total energy (kinetic plus potential) varies by the law

$$E = \frac{m_2 V^2}{2} \frac{\eta^2}{\xi^2} \sin^2 \left(\frac{\omega_1 - \omega_2}{2} t \right). \quad (3)$$

For $m_2 = m_1$, the expression for the total energy has the form

$$E_0 = \frac{m_1 V^2}{2} \sin^2 \left(\frac{\omega_1^0 - \omega_2^0}{2} t \right). \quad (4)$$

Let us take a ratio between the energies for the quarter of the oscillation period corresponding to the frequency $(\omega_1^0 - \omega_2^0)/2$:

$$f(\eta) = \frac{E}{E_0} = \frac{\eta^2}{\xi^2} \frac{m_2}{m_1} \sin^2 \left(\frac{\pi}{2} \frac{\omega_1 - \omega_2}{\omega_1^0 - \omega_2^0} \right).$$

Substituting the expressions for frequencies (1) and (2) into the function $\sin^2 \left(\frac{\pi}{2} \frac{\omega_1 - \omega_2}{\omega_1^0 - \omega_2^0} \right)$, we can see that this function approximates a unity for the range $\eta = 1.62$ – 3.73 , which is typical of the carbonates we studied, and the expression $f(\eta)$ can be written in the form

$$f(\eta) = \frac{E}{E_0} = \frac{\eta^2}{\xi^2} \frac{m_2}{m_1} = \frac{\eta}{\xi^2}. \quad (5)$$

This function (Fig. 5) has a peak at $\eta = m_1/m_2 = 1$ and is symmetrical with respect to the substitution $\gamma = 1/\eta$, that is $f(\eta) = f(1/\eta)$. This means that the process of energy transfer is controlled by the ratio of these masses alone and is independent of the fact which of the masses transfers or receives the energy.

Assuming that the thermal conductivities of materials with an isovalent replacement are proportional to this function, we can write

$$\lambda = \lambda_0 f(\eta), \quad (6)$$

where λ is the thermal conductivity of the material under study, and λ_0 is a constant having a sense of the thermal conductivity of a material, the cation and anion masses of which are equal. We derived equation (6) proceeding from the assumption that at high frequencies energy is transferred from one atom to another by way of beating-type oscillations rather than by elastic waves. The real behavior of the thermal

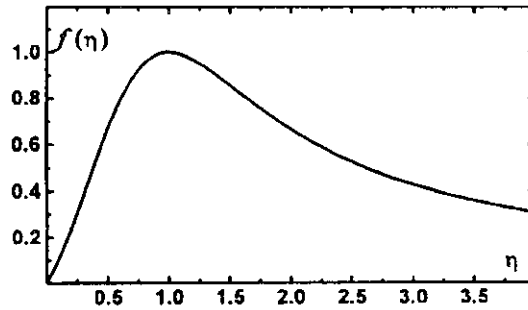


Fig. 5

Plot of function $f(\eta) = \frac{\eta}{1 - \eta + \eta^2}$.

conductivity of isoivalent replacement series is fairly well described by the equation we derived. Figure 2 shows a curve calculated using equation (6), where $\lambda_0 = 6.7 \text{ W/(m}\cdot\text{K)}$, and with the substitution of the argument, $\eta \rightarrow p\bar{M}/m_a - 1$, where p is the number of atoms in the compound, \bar{M} is the mean atomic weight, and m_a is the anion mass.

It is important to investigate one more factor affecting thermal conductivity, namely, changes in the constants of interaction between the atoms caused by changes in the distances between the atoms inside a unit cell and between the anion cores themselves. Special attention should be given to the point concerning the effect of structural changes upon the value of thermal conductivity. For instance, the thermal diffusivity of aragonite is substantially lower than that of calcite (see Fig. 1), even though the chemical compositions of these minerals are identical, and the density of aragonite is even higher than that of calcite.

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