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Measurement and Analysis of Thermophysical Properties of Diorites in the Temperature Range from 253 to 333 K

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Thermal conductivity and thermal diffusivity are simultaneously measured for a collection of diorite samples taken from Shewa-Shahbaz Garhi volcanic complex near Mardan, Pakistan by using the transient plane source (TPS) technique. The temperature dependence of the transport properties of these samples is studied in the temperature range from 253 to 333 K. Different relationships for the temperature dependence of the thermal conductivity and thermal diffusivity are tested. The samples are also characterized by their chemical composition, density, porosity, and specific gravity at room temperature and atmospheric pressure. Theoretical calculation of the specific gravity parameter based on the chemical composition is in good agreement with the experimental observation. No correlation was found for the temperature dependence of the thermal transport behavior on porosity, chemical composition, and density.

KEY WORDS: density; diorites; specific gravity; thermal conductivity; thermal diffusivity.

1. INTRODUCTION

The knowledge of the thermophysical properties of rocks is important in many fields like the compressive strength aids in the selection of the shell materials for rock filled dams, for locating geothermal reservoirs, and for

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underground disposal of nuclear waste. Density is the basis for the selection of the most durable protective facing for earth dams. Thermal studies are also used in mineralogy and petrography to analyze minerals and determine composition of rocks. Igneous rocks are formed [1,2] by the cooling of magma and are primary rocks (granite, diorite, basalt, dunite). They are conventionally subdivided according to their silica content, into granite ($SiO_2 > 65\%$), diorite ($SiO_2 = 65$–52%), basalt ($SiO_2 = 52$–40%), and dunite ($SiO_2 < 40\%$). This paper reports the chemical composition, density, porosity, specific gravity, and thermal transport properties of 13 diorite samples in the temperature range from 253 to 333 K.

2. EXPERIMENTAL TECHNIQUES AND SAMPLE CHARACTERIZATION

All the samples were obtained from the Shewa-Shahbaz Garhi volcanic complex, near Mardan, Pakistan. These samples were then cut into rectangular shapes. Each sample consisted of two identical rectangular slabs of approximately $0.045\,m \times 0.045\,m \times 0.025\,m$. The surfaces of these samples were polished to provide good thermal contact with the TPS-sensor and to minimize thermal contact resistance [3]. The chemical composition was analyzed by using the X-ray fluorescence technique and is given in Table I. The density, porosity and specific gravity (specific gravity represents the ratio of the mass of a unit volume of a material at a stated temperature to the mass volume of gas-free distilled water) [4] of the samples were measured by using American Society for Testing and Materials (ASTM) standard methods [5] and details have been published by the present authors [6]. In this paper only the data for these parameters along with the calculated results for the specific gravity are mentioned. Table II provides the samples characterization. The transient plane source (TPS) technique [7] was chosen to measure the thermal transport properties of these materials because it allows measurements without any disturbance from the interfaces between the sensor and the bulk samples. Also, simultaneous measurements of thermal conductivity, thermal diffusivity, and heat capacity per unit volume are possible [3]. In this technique, a TPS element is used both as a constant heat source and sensor of temperature. For data collection the TPS element (20 mm diameter) sandwiched between two specimen halves in a bridge circuit [8,9] was used. When a sufficiently large amount of direct current is passed through the TPS element, its temperature changes and there is a voltage drop across the TPS element. By recording this voltage drop for a particular time interval, detailed information about the thermal conductivity (λ) and thermal diffusivity (κ) of the test specimen is obtained. The heat capacity per unit volume (ρC_p) is then calculated from the relation,

Table I. Chemical Composition of Diorite Samples in Mass %

Sample	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5
SSG-D1	55.25	0.08	24.28	1.13	1.02	0.41	0.01	0.74	13.83	4.71	0.02
SSG-D2	57.03	0.27	23.11	0.87	1.40	0.10	0.25	1.21	10.13	5.55	0.04
SSG-D3	58.30	0.11	21.34	0.67	1.07	0.08	0.06	0.68	11.16	6.52	0.02
SSG-D4	58.63	0.72	20.68	1.19	1.91	0.20	0.73	2.26	7.92	5.64	0.12
SSG-D5	58.77	0.94	19.08	1.82	2.91	0.21	1.21	2.86	6.88	5.16	0.25
SSG-D6	58.77	1.53	17.28	2.98	3.28	0.17	1.78	4.06	5.20	4.54	0.42
SSG-D7	58.87	0.16	21.92	1.12	1.80	0.13	0.08	0.67	10.28	4.95	0.01
SSG-D8	60.83	0.84	18.6	1.87	2.06	0.17	0.45	2.10	5.50	7.52	0.05
SSG-D9	61.63	0.58	19.47	1.03	1.64	0.16	0.28	1.25	7.99	5.93	0.04
SSG-D10	61.77	0.83	18.24	1.72	1.92	0.15	0.43	1.95	5.51	7.43	0.07
SSG-D11	61.87	0.52	19.33	1.21	1.92	0.12	0.23	1.45	7.27	6.04	0.04
SSG-D12	62.17	0.46	18.90	1.16	1.86	0.10	0.23	1.79	7.58	5.73	0.03
SSG-D13	63.93	0.46	18.63	1.38	1.52	0.11	0.35	1.23	7.09	5.38	0.12

Table II. Characteristics of Diorite Samples at 298 K and Atmospheric Pressure. (Experimental data are taken from Ref. [6].)

Sample No.	Specific gravity		Density	Porosity
	measured ±0.003	calculated	(10^3 kg·m^{-3}) ±0.002	(%)
SSG-D1	2.624	2.644	2.615	0.335
SSG-D2	2.599	2.646	2.594	0.167
SSG-D3	2.603	2.643	2.599	0.162
SSG-D4	2.608	2.666	2.595	0.490
SSG-D5	2.718	2.702	2.708	0.353
SSG-D6	2.838	2.751	2.827	0.397
SSG-D7	2.589	2.646	2.583	0.234
SSG-D8	2.723	2.669	2.411	0.469
SSG-D9	2.627	2.648	2.622	0.206
SSG-D10	2.621	2.663	2.612	0.347
SSG-D11	2.624	2.652	2.613	0.424
SSG-D12	2.554	2.653	2.544	0.413
SSG-D13	2.706	2.649	2.697	0.358

$$\rho C_p = \frac{\lambda}{\kappa}, \tag{1}$$

where ρ is the density of the sample.

Advantages of the TPS method include the simplicity of the technique and its applicability to these insulating materials [9,10]. The thermal conductivity, thermal diffusivity, and heat capacity per unit volume of all diorite samples at different temperatures were measured at atmospheric

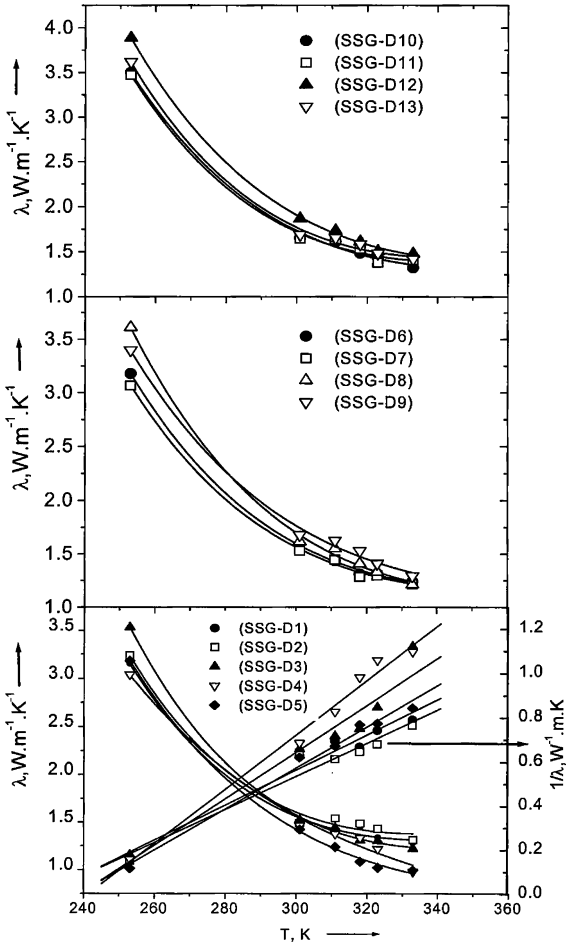

Fig. 1. Temperature dependence of thermal conductivity along with the fit (————) to least squares polynomial of second order and $1/\lambda = P + QT$. Estimated uncertainties in λ are 5%.

pressure and are given in Figs. 1 and 2. Every measurement was repeated five times under identical conditions, and the mean values are shown in the figures. Taking into consideration the uncertainties of the technique and the standard deviations of the measurements [6], the estimated uncertainties of the thermal conductivity and thermal diffusivity measurements are approximately 5 and 7%, respectively. The uncertainties in the volumetric heat capacity are about 10%.

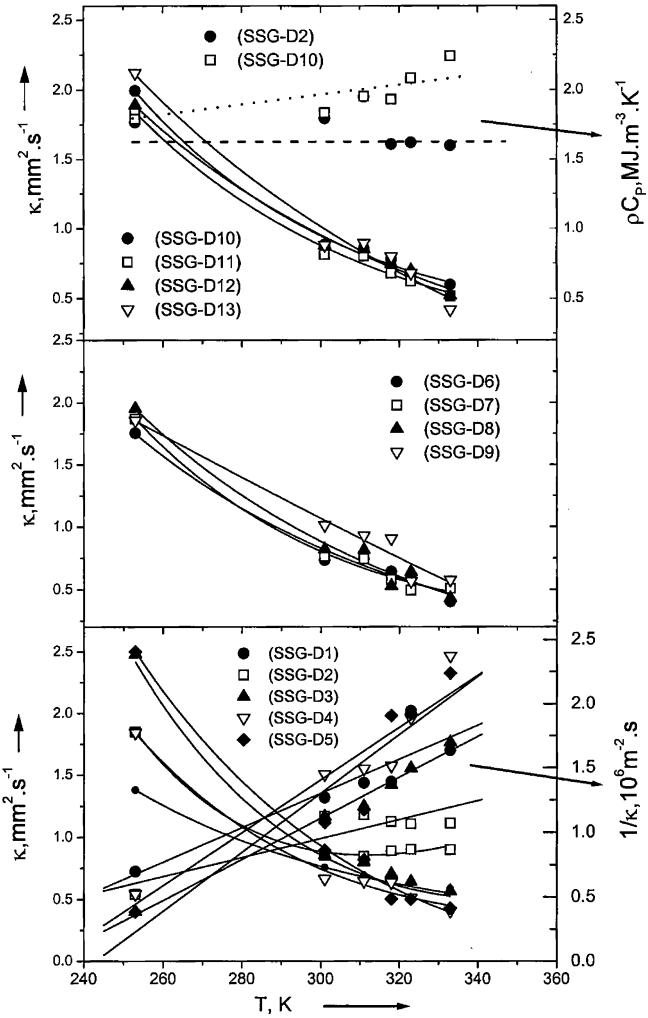

Fig. 2. Temperature dependence of thermal diffusivity along with the fit (————) to least squares polynomial of second order and $1/\kappa = R + ST$. Estimated uncertainties in κ and ρC_p are about 7 and 10%, respectively.

3. RESULTS AND DISSCUSSION

The thermal properties of solid materials depend upon their structure, chemical composition, density, porosity, and specific gravity. Specific gravity, density and porosity are grouped as density-related properties of rocks.

Discussion on the density-related and thermal transport properties is covered in the following sections.

3.1. Density-related Properties

Density-related properties have no connection with any external factor and so are not mechanical. They must, however, be considered first before any other property of the rocks can be studied. Numerous attempts have been made to use specific gravity as a predictor of other rock properties [2]. For example, there may be a relationship between density and rock composition or porosity. Young and Olhoeft [11] tested the relationship between specific gravity and the chemical composition of rocks. The objective apparently was to develop a test that would assist in a more accurate identification of rock types. They found that the Felsic-mafic index (F) provides a better correlation curve than the silica content when attempts are made to correlate specific gravity and chemical composition. However, the correlation becomes less useful when the rock is more felsic than quartz monzonite. The useful curve they offer is

$$\text{Specific gravity} = 2.643 + 0.444\mathrm{e}^{-F/4}, \tag{2}$$

$$\text{where} \quad F = \frac{\mathrm{SiO_2} + \mathrm{Na_2O} + \mathrm{K_2O}}{\mathrm{FeO} + \mathrm{Fe_2O_3} + \mathrm{CaO} + \mathrm{MgO}}. \tag{3}$$

Using this relation and the data of Table I, the specific gravities of all the diorite samples were calculated and these are tabulated in Table II. There is good agreement between the observed and calculated specific gravity parameter.

Density is an intrinsic property of rocks that denotes the relationship between its mass and unit volume. It is used as an index property or an independent variable to predict other rock properties and is difficult to characterize because this parameter can be affected by temperature, pressure, and the amount and type of fluid saturation. Table II shows the measured values of diorites. All dependent factors vary slightly due to a difference in the chemical composition of SiO_2. The density values of these samples lie between (2.411 and 2.827) $\times 10^3\,\mathrm{kg \cdot m^{-3}}$. The specific gravity of all these samples lies between 2.554 and 2.838. The storage capacity of porous rocks is referred to as the porosity and is that fraction of the bulk volume of rocks available for the storage of the fluid. The porosity of the rocks depends on the shape and size of the grains and on the degree of their sorting and packing [2]. The porosity of these samples varies from 0.162 to 0.490%. This variation in porosity depends on the composition of the sample, since in the diorites the dominant mineral is

SiO_2, which accounts for approximately 55% or above of the materials in the samples. Again, these values are comparable with those from previous reports [1,2].

3.2. Temperature Dependence of the Thermal Transport Properties

The measured thermal conductivity, thermal diffusivity, and heat capacity per unit volume of all the diorite samples at different temperatures are plotted in Figs. 1 and 2. The thermal conductivity ranges from 1.4 to $1.9\,W{\cdot}m^{-1}{\cdot}K^{-1}$ at 301 K. The decrease in the thermal conductivity with increasing porosity, within experimental uncertainty, is in complete agreement with the reported results of Woodside and Messmer [12], Sugawara and Youshizawa [13], and Shabbir et al. [14]. The thermal diffusivity and volumetric heat capacity per unit volume at 301 K ranged from 0.6×10^{-6} to $1.1 \times 10^{-6}\,m^2{\cdot}s^{-1}$ and from 1.0 to $2.3 \times 10^6\,J{\cdot}m^{-3}{\cdot}K^{-1}$, respectively. From Figs. 1 and 2, it is noticed that the change in thermal diffusivity is similar to that of thermal conductivity as it depends directly upon the thermal conductivity, whereas the heat capacity remains constant within experimental uncertainty. Sample graphs are shown in Figs. 1 and 2.

It is also evident from Fig. 1 that the thermal conductivity of all the samples decreases with an increase in temperature. Also, all the samples follow the same trend. This can be traced back to their respective similar mineral contents (Table I). Theoretically, the thermal energy in solids consists of waves that travel with the velocity of sound. They are therefore capable of transporting energy. From the kinetic theory of gases we have [15]

$$\lambda = \frac{1}{3} C V_{\mathrm{ph}} \ell, \tag{4}$$

where C is the heat capacity, V_{ph} is the phonon velocity, and ℓ is the mean free path.

Under harmonic approximation the waves travel free without attenuation, giving infinite conductivity. In reality, anharmonic terms, impurities, imperfections, and the grain size limit their path [16]. If we consider the lattice waves as a phonon gas and in the light of Eq. (4), it seems that with an increase in temperature, the mean free path of the crystalline materials decreases, which agrees with our observation of the decrease of the thermal conductivity and thermal diffusivity with an increase of temperature. For the diorites investigated, various ways of data processing were tested. Starting from the general Eucken's rule [17],

$$\lambda = a_1 T^{-1}, \tag{5}$$

where a_1 is the proportionality constant and depends on the structure and mass of the material under consideration [16]. This law is normally applicable to simple inorganic compounds. A more complex relation of the following type is often found to be workable:

$$\lambda = a_2 T^{-n}, \quad 1.05 \leqslant n \leqslant 1.15. \tag{6}$$

The values $n > 1$ are attributed to the volume effect [16]. The above relations did not fit well to these structurally complex materials, which might be due to the fact that these models are good for those solids, which have alkali and halogen ions of nearly equal masses. Such crystals can be regarded as monatomic. The decrease in thermal conductivity with increasing different masses, which had already been noted by Eucken and Kuhn [18], was ascribed by Blackman [19]. The increase in the resistance is probably the result of the additional U-processes arising from the extra zone boundaries associated with the mass difference [20]. The variation becomes more pronounced as the temperature is increased. This is the result of the additional resistance arising from higher order anharmonities.

For the analysis of our data, an additional temperature-independent term was added to the thermal resistivity $R = 1/\lambda$ to Eucken's rule as

$$\frac{1}{\lambda} = \mathrm{P} + \mathrm{Q}T. \tag{7}$$

The physical justification of this term is the existence of numerous additional scattering centers for phonons in rocks, caused by structural and chemical imperfections and the influence of the grain boundaries. For the diffusivity, analogous equations were assumed as

$$\frac{1}{\kappa} = \mathrm{R} + \mathrm{S}T. \tag{8}$$

The results obtained using the above equations are tabulated in Table III. The correlation functions for thermal conductivity (r_λ) and thermal diffusivity (r_κ) are also listed. The data appear to fit very well. ρC_p can be calculated with the help of Eq. (1). It remains almost constant within experimental uncertainties (Fig. 2). From a knowledge of these thermal transport properties, it is possible to understand the mechanism of heat flow through these materials and therefore one can easily select a material for a particular application.

Table III. Fitting Parameters P, Q, R, and S for the Thermal Conductivity $\lambda(T)$ and the Thermal Diffusivity $\kappa(T)$ as represented by Eqs. (7) and (8); r_λ and r_κ are the Respective Correlation Coefficients

Sample No.	P ($W^{-1}\cdot m^{-1}\cdot K^{-1}$)	Q ($10^{-3}\,W^{-1}\cdot m^{-1}$)	r_λ	R ($10^6\,s\cdot m^{-2}$)	S ($10^4\,s\cdot m^{-2}\cdot K^{-1}$)	r_κ
SSG-D1	−1.14	5.86	0.983	−2.78	1.38	0.906
SSG-D2	−1.067	5.53	0.973	−1.29	0.76	0.878
SSG-D3	−1.66	7.78	0.970	−3.80	1.65	0.994
SSG-D4	−1.98	9.05	0.993	−4.91	2.12	0.951
SSG-D5	−1.44	6.86	0.994	−5.75	2.37	0.933
SSG-D6	−1.28	6.35	0.996	−4.52	1.96	0.903
SSG-D7	−1.27	6.35	0.994	−4.31	1.89	0.961
SSG-D8	−1.18	5.84	0.995	−4.68	2.00	0.908
SSG-D9	−1.43	6.74	0.997	−3.26	1.46	0.872
SSG-D10	−1.18	5.82	0.995	−3.07	1.40	0.980
SSG-D11	−1.10	5.53	0.982	−3.60	1.61	0.970
SSG-D12	−1.11	5.44	0.995	−3.38	1.51	0.943
SSG-D13	−1.08	5.41	0.990	−4.48	1.89	0.850

4. CONCLUSIONS

A collection of diorite samples obtained from the Shewa-Shabaz Ghari volcanic complex were characterized by the chemical composition and density related properties like density, porosity and specific gravity at ambient temperature and pressure. The thermal conductivity and thermal diffusivity have been measured simultaneously for these samples by the use of the TPS technique. The temperature range of the transport properties was 253 to 333 K. Both the thermal conductivity and thermal diffusivity decrease with an increase in temperature, and ρC_p remains almost constant within experimental uncertainty. Different relationships for the temperature dependence of thermal conductivity and thermal diffusivity are also tested. No correlation is found between the temperature dependence of the thermal transport behavior on porosity, chemical composition, and density.

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