Recent progress in the experimental studies on the kinetic properties in minerals

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A R T I C L E   I N F O

A B S T R A C T

This article reviews the current status of experimental studies on some of the kinetic properties of minerals that have been covered by papers presented in this special volume. Properties discussed include plastic deformation, kinetics of phase transformations, thermal conductivity and electrical conductivity. In addition to a brief historical review, some discussions are presented on the issues on plastic deformation and electrical conductivity where results from various groups show some discrepancies.

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1. Introduction

Transport properties of minerals have an important influence on the dynamics and evolution of Earth and other terrestrial planets. Some have direct influence on mantle convection and other key processes in Earth and others provide important information on thermo-chemical structures of Earth, thereby indirectly helping us to understand geodynamics. Among the topics covered by the papers published in this chapter, rheological properties, kinetics of phase transformations and thermal conductivity belong to the first category, and electrical conductivity belongs to the second category.

In this introductory chapter, I will provide a brief review of studies of each topic and discuss the significance of reported study and some future directions.

2. Plastic deformation (Li et al., 2008; Mei et al., 2008; Nishihara et al., 2008)

Most of the dynamic processes of Earth are driven by mantle convection, a process that is possible because minerals in the deep interior of Earth behave viscously rather than elastically. However, "viscous", namely rheological, properties are sensitive to a number of parameters and can change, by orders of magnitude, due to the variation of various physical and chemical parameters in

Earth. Consequently, understanding the rheological properties of minerals under the conditions of Earth's interior is critical to the understanding of dynamics of Earth's interior.

Experimental studies play an important role in the study of plastic deformation, but the experimental approaches have major challenges for a couple of reasons. In any experimental study of plastic deformation, applications of experimental results to geological problems are not straightforward (for reviews on plastic properties see, e.g., Karato, 2008; Poirier, 1985). Firstly, complications include the facts that (1) it is impossible to reproduce geological strain-rates in the laboratory and therefore a large extrapolation is needed to apply the laboratory data of plastic deformation to Earth's interior, (2) the presence of multiple deformation mechanisms, each of which dominates under particular conditions, and consequently, one needs to identify the operating mechanisms in the lab and in Earth (lab results can be applied to Earth only when the mechanisms of deformation are the same), and (3) because plastic properties are sensitive to many parameters, the influence of many parameters must be explored (e.g., stress, strain, temperature, pressure, water content, grain-size).

Secondly, quantitative studies of plastic properties are difficult under high-pressure conditions because of the difficulties in the controlled generation of deviatoric stress (strain) and their measurements. Unequivocal data that have addressed issues listed above were available only below P (pressure) ~ 0.5 GPa using a gas-medium deformation apparatus with an internal load cell (Paterson, 1990). The advantage of using this type of apparatus is the high resolution in stress measurements and homogeneous temperature distribution that allows a precise control of thermo-

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chemical conditions. However, because of the small pressure range, characterization of pressure effects is very difficult and even more seriously, results below ∼0.5 GPa on the influence of water cannot be extrapolated to higher pressures because of the change in the thermodynamic properties of water (Karato, 2006). In addition, rheological properties of minerals that are only stable above ∼1 GPa cannot be investigated. Recognizing these difficulties, several attempts have been made to extend the pressure range of quantitative rheological studies. Two different types of high-pressure apparatus are used or developed. For example, the existing diamond anvil cell (DAC) can be used for deformation studies without much modification because compression using DAC (without soft pressure medium) inevitably generates deviatoric stress (Kinsland and Bassett, 1977; Sung et al., 1977). This approach has recently been expanded to higher pressures and with a broader range of X-ray diffraction techniques including *in situ* texture measurements (Mao et al., 1998; Wenk et al., 2004). Major advantages of a DAC approach are (1) the greater pressures accessible for deformation studies, and (2) the better access to various spectroscopic techniques. However, the current technique of deformation experiments with DAC does not allow us to investigate the key details discussed above (influence of temperature, stress, strain, etc.) and the applicability of results from DAC deformation experiments to Earth's interior is highly limited. An alternative approach is to use large-volume high-pressure apparatus. Two types of deformation apparatus have been designed (deformation DIA (DDIA) and rotational Drickamer apparatus (RDA); see Karato and Weidner, 2008) and two papers in this volume present results using these new equipment. Nishihara et al. (this issue) report new results on the rheological properties of olivine and wadsleyite to $P \sim 15$ GPa, and $T \sim 1800$ K using RDA, and Mei et al. (this issue) report new results on plastic deformation of MgO to $P \sim 6$ GPa and $T \sim 1473$ K using DDIA. Li et al. report the results of application of these new *in situ* high-pressure, temperature deformation experiments using DDIA combined with the synchrotron facility to investigate the processes by which a melt phase penetrates into a solid matrix and the influence of such a process on the mechanical properties.

Although much progress in experimental studies of plastic deformation has been made, there are many issues that need to be addressed. First, in all of these new high-pressure deformation experiments, the use of high intensity X-rays from a synchrotron facility plays a key role. However, by applying these techniques with DDIA, Li et al. (2004) (see also Chen et al., 2006; Weidner et al., 2004) recognized that a commonly used theory by Singh (1993) is inadequate in analyzing the radial X-ray diffraction data to determine the deviatoric stress. A new theory must be developed that includes the influence of plastic deformation in stress distribution in a polycrystal. Second, the pressure range of quantitative rheological studies with DDIA or RDA is still limited (<20 GPa). There is a need for technical development to extend the maximum pressure for quantitative rheological experiments beyond 24 GPa (pressure at the 660-km discontinuity). Also there have been large discrepancies among different studies that are likely due to the complications in the study of plastic deformation. For example, there is a large range of activation volumes for dislocation creep in olivine (the reported values range from ∼0 to ∼27×10^{-6} m^3/mol). Likely causes for this large discrepancy are the influence of transient creep in some of the low-strain experiments, the influence of grain-size and water content. All of these issues need to be carefully characterized to obtain robust results on rheological properties under deep mantle conditions. Through large-strain deformation of olivine polycrystals experiments under truly dry conditions (Kawazoe et al., 2008) determined the activation volume of $(15–20) \times 10^{-6}$ m^3/mol for power-law creep.

3. Kinetics of phase transformations (Kubo et al., 2008)

Kinetics of phase transformation plays an important role in our understanding of geodynamics. First, kinetics of phase transformations, particularly under the relatively low-temperature conditions in a subducting slab, controls the degree to which the metastable presence of a given mineral might occur. The persistence of a metastable mineral has an important influence on the density distribution and hence the dynamics. Second, the kinetics of phase transformation controls the microstructure, particularly grain-size, after a transformation that has an important bearing on the rheological properties.

Vaughan and Coe (1981) and Rubie (1984) discussed the possible role of grain-size reduction on the rheological properties. Detailed studies of kinetics of phase transformations have been made in the subsequent years (e.g., Rubie and Ross, 1994) and Riedel and Karato (1997) presented a theoretical analysis on grain-size evolution using the Avrami theory and numerical modeling. Kubo et al. (1998, 2000, 2002) conducted detailed studies including the influence of water. Kubo et al. (this issue) present new results on the phase transformation of garnet that have important implications for the dynamics around the 660-km discontinuity.

4. Thermal conductivity (Hofmeister, 2008)

Thermal conductivity is an important property of minerals that plays an important role in many aspects of geodynamics. A particularly important is the fact that thermal conductivity controls the temperature gradient in a thermal boundary layer. For a given heat flux, the temperature gradient and hence a temperature change across a thermal boundary layer is inversely proportional to thermal conductivity. Particularly important are the temperature change across deep thermal boundary layer such as the D″ layer. Brown (1986) pointed out an important effect of pressure to change thermal conductivity, and Hofmeister (1999) presented a new theoretical analysis for the temperature (and pressure) dependence of thermal conductivity.

A particularly important issue in thermal conductivity is the evaluation of contribution from radiative transfer. However, both experimental and theoretical studies of thermal conductivity are complicated including the influence of sample and anvil contact and of grain-boundaries. Hofmeister (this issue) addresses some of these issues in the experimental study of thermal conductivity.

5. Electrical conductivity (Yoshino et al., 2008b)

Electrical conductivity does not have any direct relevance to the dynamics of Earth's interior. Any geodynamic modeling of mantle dynamics can be done without knowing electrical conductivity. However, the study of electrical conductivity is important because it provides a key to infer some of the important parameters in Earth's interior. Most mantle minerals are insulators or semi-conductors and therefore electrical conductivity in minerals is sensitive to temperature. Consequently, a comparison of geophysically determined electrical conductivity with laboratory data provides constraints on temperature in Earth (and other planets). Such studies were conducted in the early 1970s (e.g., Duba, 1972; Duba and Ringwood, 1973). However, results of marine geomagnetic sounding measurements (e.g., Filloux, 1982) showed that the temperature inferred from electrical conductivity in the asthenosphere near mid-ocean ridges significantly exceeds the solidus of the upper mantle rocks and therefore it was considered that partial melting is required to explain the data (Shankland et al., 1981). However, Shankland et al. (1981) also noted that a partial melt model would require a rel-

atively large melt fraction (several %) that is difficult to maintain in a dynamic Earth because of effective compaction. In addition, recent petrological and geochemical studies show that the partial melting away from ridges is caused by the presence of water and consequently, the degree of melting is likely limited to <0.2% (for a review, see Langmuir et al., 1992). Consequently, one needs a special mechanism to accumulate the melt to increase the melt fraction if a high electrical conductivity were to be attributed to partial melting. In order to resolve this problem, Karato (1990) proposed that hydrogen (proton) may enhance electrical conductivity based on the experimental data on the solubility and mobility of hydrogen in olivine. Another issue is the electrical conductivity in deep mantle minerals. Banks (1969) (see also Utada et al., 2003) showed that electrical conductivity increases significantly with depth. Also three-dimensional distribution of electrical conductivity has been determined (Ichiki et al., 2006).

Consequently, the main thrusts in the experimental studies of electrical conductivity have been to address the issue of influence of hydrogen and of phase transformations. The first study to test the hypothesis of hydrogen effect was Huang et al. (2005) that not only confirmed the hypothesis of hydrogen-enhanced conductivity but also showed that earlier results by Xu et al. (1998) on the role of olivine-wadsleyite–ringwoodite transformation were affected by the unrecognized role of hydrogen. Similar studies were conducted by Yoshino et al. (2006) on wadsleyite and ringwoodite, and Wang et al. (2006) and Yoshino et al. (2006) showed the enhanced electrical conductivity in olivine by hydrogen. Although these results largely confirm the hypothesis of hydrogen-enhanced conductivity, the evaluation of the hydrogen content from electrical conductivity is not straightforward. For example, whereas Wang et al. (2006) estimated ∼0.01 wt% of water in the asthenosphere from electrical conductivity of olivine, Yoshino et al. (2006) argued that the influence of hydrogen is weaker and cannot explain the observed electrical conductivity if a geochemically inferred value of water content is used and suggested the influence of partial melting as discussed by Shankland et al. (1981). Similarly, although Huang et al. (2005) inferred ∼0.1–0.2 wt% water in the transition zone from electrical conductivity, Yoshino et al. (2008a) discussed that the observed conductivity profile can be attributed to dry (water-free) mantle. A paper by Yoshino et al. (this volume) also suggested for a large contribution of the polaron mechanism in majorite garnet. The competition between polaron and proton is delicate and there are some differences among different studies that lead to important differences in the estimated water contents. Differences include the difference in activation energy for hydrogen-related conduction and the functional form to parameterize the dependence of conductivity. Note, however, that the distinction among various mechanisms of conduction by Yoshino et al. (this issue) is made only by the difference in activation energy. Activation energy provides only weak constraints on conduction mechanism. Rather than (in addition to) activation energy, the dependence of conductivity on chemical environment such as water content (fugacity) and oxygen fugacity should be used to identify the dominant conduction mechanism(s). The exact causes for differences are not well understood but can include differences in (i) the frequency range of impedance measurements, (ii) the interpretation of FT-IR absorption spectra, and (iii) the parameterization of the influence of hydrogen on electrical conductivity. When ionic conduction is an important mechanism of electrical conductivity, then there is a bias in the measured results if one uses only low frequency data. Such a systematic bias has been documented for some minerals (e.g., garnet and wadsleyite). Therefore it is likely that some part of discrepancy between the results from two laboratories can be attributed to the difference in the frequency range used.

Also the interpretation of FT-IR absorption spectra is not straightforward and there are technical issues in the interpretation of FT-IR results by Yoshino and his colleagues. A report included in this volume (Yoshino et al.) provides a new data set for "dry" majorite garnet, but the exact water contents in their samples are not well constrained. The FT-IR spectrum shown in their paper shows a large broad absorption peak but the authors interpret it as "dry" (i.e., water-free). Similarly, the "dry" wadsleyite investigated by Yoshino et al. (2008a,b) contains ∼1000 ppm H/Si of hydrogen. I conclude that the argument for "dry" transition zone minerals is subject to large uncertainties. Further studies are definitely needed to place better constraints on the water content in the mantle from electrical conductivity.

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