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Characteristics of Perovskite-Related Materials [and Discussion]

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Characteristics of perovskite-related materials

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Oxides with perovskite structure show characteristic features of their physical behaviour that can be relevant for the understanding of the mantle material (MgFe)SiO_3. Perovskites distort locally, and four different mechanisms have been found: tilt of octahedral complexes, off-centring of the octahedrally coordinated cation, distortion of the octahedral cage and off-centring of the 12-fold coordinated site. These deformations usually lead to structural instabilities related to phase transitions, extremely sluggish kinetic behaviour even leading to pseudo-glasses and polaronic transport. All these properties depend sensitively on the oxygen fugacities, defect densities and the rheology of the system. There is some evidence that the predicted structural phase transitions and glass states occur in $CaSiO_3$ whereas no structural instability has yet been reported in $MgSiO_3$.

Introduction

Materials with perovskite structure, or topologically closely related structures, have been of central interest to many solid-state scientists over the past three decades. Typical examples for research in physics range from the investigation of critical phenomena during structural phase transitions (e.g. in $SrTiO_3$ and $PrAlO_3$) to superconductivity in Cu-containing phases. Chemists are mainly interested in transport properties and defect structures (e.g. in WO_3 and related bronzes) and engineers and materials scientists have focused their research on electronic switching and the characterization of the properties of ceramic material. Research on perovskite structures has only recently been extended to (MgFe)SiO_3, a material that is thought to make up most of the lower Earth mantle. The relatively new research efforts on (MgFe)SiO_3 can potentially profit from the knowledge of the physical and chemical behaviour of other perovskite structures. It is the purpose of this paper to outline some of the typical materials properties of well-known oxides with perovskite structure.

Structural instabilities

The most outstanding feature of the perovskite structure is that its topology (i.e. the principal arrangement of atoms) is thermodynamically extremely stable whereas its actual crystal structure (i.e. the actual positions of the atoms) appears to be very unstable (Salje 1976*a*, *b*). This structural instability leads almost invariably to structural deformations that destroy the high symmetric atomic arrangements that would occur in cubic material with the space group *Pm*3*m*, (figure 1). In fact, virtually all perovskite structures are low symmetric, having lowered their symmetry via structural phase transitions. There are four typical deformation patterns, as shown in figure 1. They consist of octahedral tilts, off-centring of the octahedra midpoint B-position, octahedral distortion and shift of the 12-fold coordinated A-position away from the

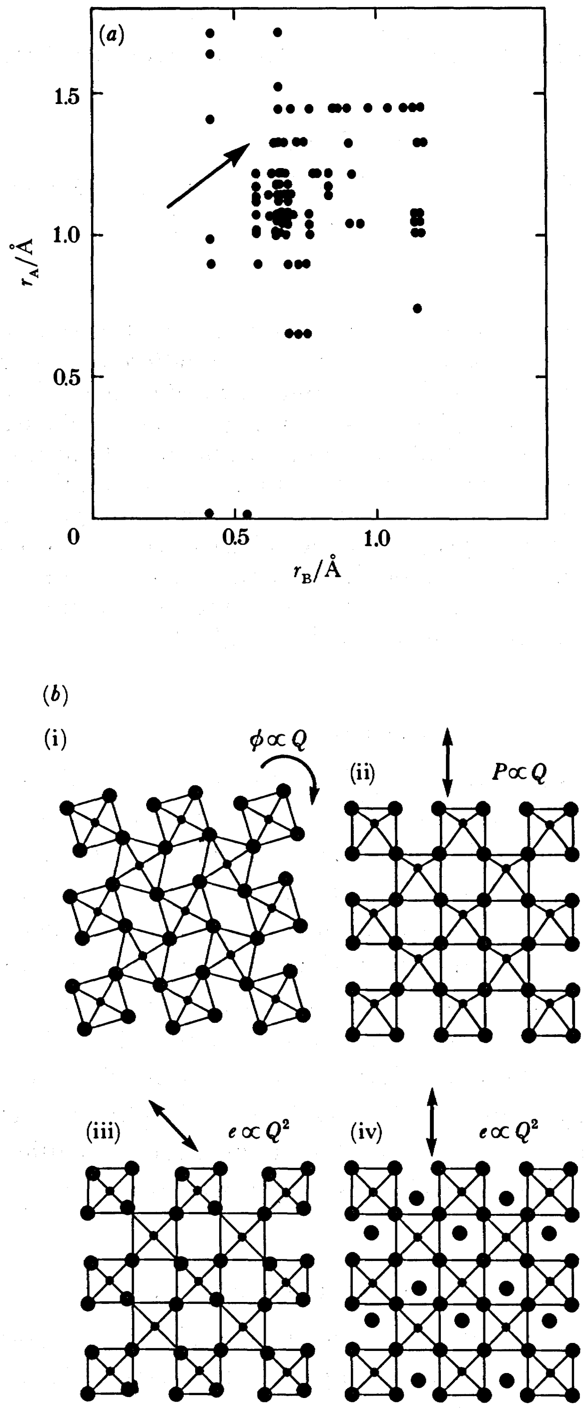

FIGURE 1. (*a*) Distribution ionic radii in various perovskites (r_A = radius of A atom, r_B = radius of B atom). The densest packing would occur for $r_A \approx 1.3$ Å, and $r_B \approx 0.56$ Å as indicated by the arrow. (1 Å = 10^{-10} m = 10^{-1} nm.) (*b*) Distortion pattern of perovskite structures: (i) tilt distortion (octahedra rotation): (ii) Slater distortion (off-centring of the B position; (iii) 'co-valent' distortion (distortion of the oxygen octahedra); (iv) off-centring of the A position. The order parameter Q is indicated in each case, note that (ii) is drawn as Γ-instability whereas all other examples are zone-boundary instabilities.

cavity centre. The crystal chemical origin for these structural distortions has been explored in great detail, both theoretically and experimentally (see, for example, Luthi & Rehwald 1981; Blinc & Zeks 1979; Muller 1986).

Changes in the external thermodynamic conditions, such as temperature, pressure, or chemical composition, lead to systematic structural variations that appear as collective movement of the atomic positions. This leads, in turn, to critical phenomena related to structural phase transitions. Such critical behaviour appears as strongly temperature dependent elastic constants, as in the case of $PrAlO_3$ (figure 2). Soft optic modes are a very common feature in tilt instabilities and phase transitions involving off-centring mechanisms (figure 3). The correlated order parameter follows mainly Landau-behaviour over a large temperature interval under non-critical conditions. Under temperature and pressure conditions close to the critical point (in the Ginzburg interval), fluctuation behaviour occurs for some perovskites (figure 4). The Ginzburg interval is, however, small enough to be ignored for most geological applications. It is important to note that all other physical parameters, such as density, spontaneous strain, specific heat, ultrasonic attenuation, domain formation and velocity of the domain walls, conductivity, ionic transport and cation ordering, are heavily influenced by the variations of this order parameter and do vary significantly, therefore, as a function of temperature and pressure (see reviews in Salje 1988*a*).

This surprising correlation between extreme topological stability and structural instability is superceded in some perovskite structures by their apparent unwillingness to complete a structural phase transition. This effect is essential for the application of many perovskite

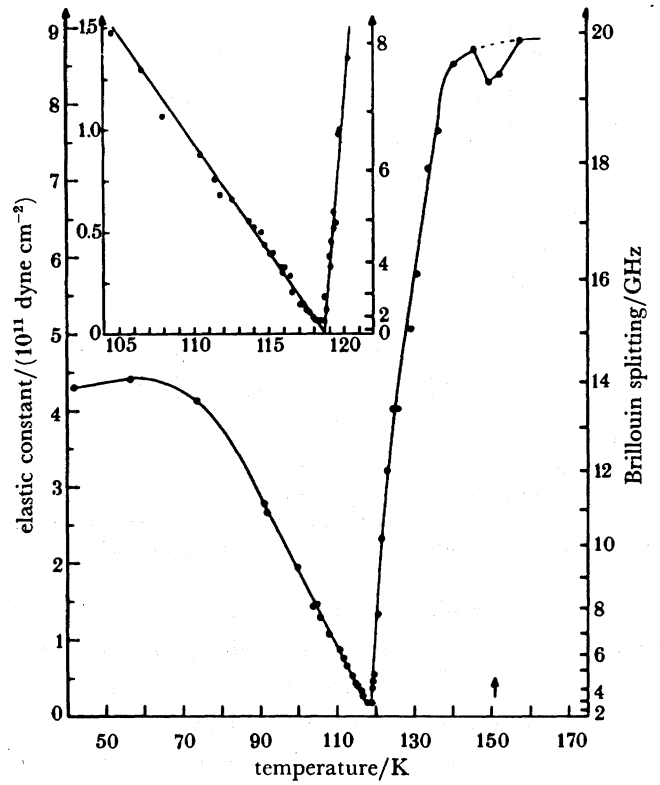

FIGURE 2. Temperature evolution of the elastic shear constant near the 118 K transition in $PrAlO_3$ (after Fleury *et al.* 1974).

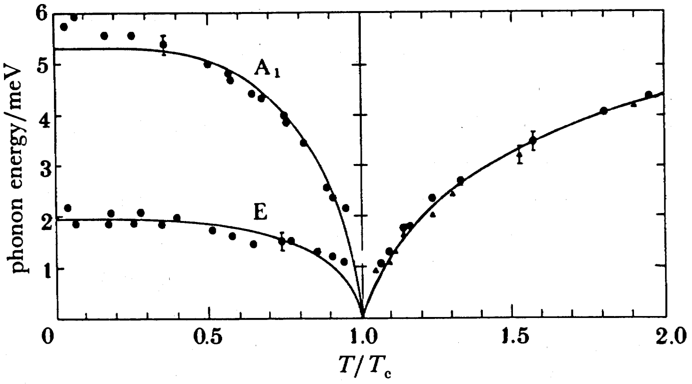

FIGURE 3. Soft-mode behaviour of $SrTiO_3$. The triply degenerate mode at $T > T_c$ splits into an A_1 mode and a double-degenerate E mode at $T < T_c$. (After Fleury *et al.* 1968; Cowely *et al.* 1969; Shirane & Yamada 1969.)

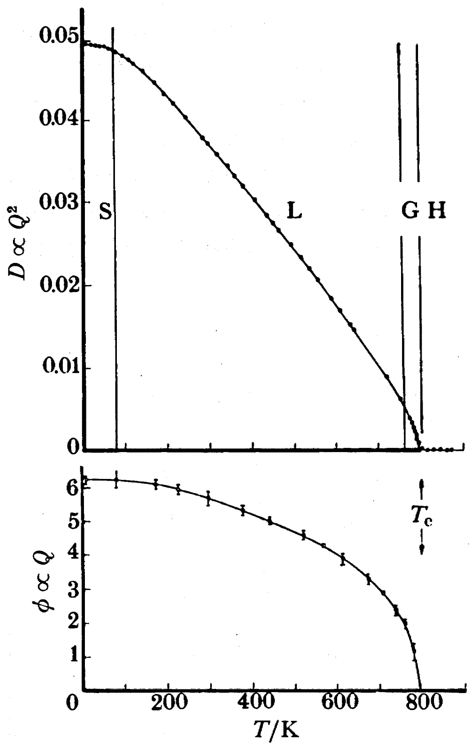

FIGURE 4. Temperature evolution of the square of the order parameter Q (top) and the linear order parameter (bottom) for $LaAlO_3$ (D in reciprocal centimetres) (for details, see Muller *et al.* 1968). The high-temperature phase is H, the three thermal régimes of the low-temperature phase are the small Ginzburg interval (G) where fluctuations are relevant, the Landau interval (L) and the saturation régime (S).

materials such as piezoelectric ceramics and slow ferroelastic switches. We can understand the sluggishness and kinetic hindrance, which prevents the phase transition occurring, from the extraordinary capacity of the perovskite structure to distort locally. Any impurity, lattice imperfection or stress field is immediately surrounded by large strain fields, which make the crystal inhomogeneous. A major role is played by oxygen deficiencies if a perovskite is placed in a slightly reducing environment. Its physical properties can thereby change dramatically. The term 'dirty ferroelectrics' has been introduced since as early as 1973 by Burns & Scott

(1973*a*) after the pioneering work of Russian groups around Smolensky and Levanyuk had penetrated western literature. The idea behind inhomogeneous, 'dirty' perovskites is that lattice imperfections couple with the order parameter of the structural phase transition. Those components of the distortion field that have the same symmetry as the order parameter act as its conjugated field and prevent the phase transition from occurring at the critical temperature. If the coupling is weak, the transition is smeared out over a large temperature interval. If the coupling is strong, the conjugate field leads to the decomposition of the crystal into interacting domains that can suppress the transition process altogether.

The most striking experimental observation for this behaviour is related to ceramic material or powdered samples. Typical examples are the commonly used $PbTiO_3$ ceramics which show no transition although the crystalline material does (Burns & Scott 1973*b*). Even more extreme is the behaviour of WO_3, which undergoes a major phase transition PI–P_c. This phase transition is completely suppressed if the material is pulverized in an agate mortar (Salje 1976*a*, *b*; Salje *et al.* 1978).

Kinetic behaviour

The tendency of the perovskite structure to distort on virtually any microscopic and submicroscopic lengthscale also leads to dramatic effects in their kinetic behaviour. Metastable structural states can often arise because the energy surface in the configuration space is highly structured. This is the outcome of many competing deformation schemes with virtually the same energy. The time dependence of a system travelling on this surface is simply defined by a generalized flow equation (Salje 1988*b*)

$$\frac{\mathrm{d}Q}{\mathrm{d}t} = -\frac{\gamma\langle a^2\rangle}{2k_\mathrm{B}T}\left(1-\frac{\zeta_\mathrm{c}^2}{\zeta^2}\mathrm{e}^{\zeta^2/2\nabla^2}\right)\frac{\delta G}{\delta Q},$$

where Q is the macroscopic order parameter, and t is the time. The other essential parameter is the ratio ζ_c/ζ, which defines the distance (in units of the correlation length) over which the order parameter Q is conserved. In a simple phase transition, Q is a non-conserved quantity and changes to zero in the high symmetric phase. In spinodal decomposition, the order parameter is conserved as averaged over several modulations, as in the case of modulated phases. Many experimental results and some theoretical concepts have been worked out for the two extreme cases $\zeta_\mathrm{c}/\zeta = 0$ and $\zeta_\mathrm{c}/\zeta = 1$ (see Salje 1988*b*) but very little is known about intermediate cases that seem to be relevant for the understanding of perovskite structures under non-equilibrium conditions.

The non-equilibrium behaviour can be characterized by a simple example. A perovskite structure under inhomogeneous stress and large local temperature variations (as typical for most experiments in diamond anvil cells) will develop a transformation pattern that follows a simple kinetic law (Salje & Wruck 1988)

$$\langle Q\rangle = L(P) = P(x)\,\mathrm{e}^{-xt}\,\mathrm{d}x,$$

where L means the Lorentz transformation, P is the probability function and t is the time. A Kirkpatrick–Sherrington glass (Kirkpatrick & Sherrington 1978) follows

$$P(x) = \frac{1}{2\pi}\left(\frac{4}{x}-1\right)^{\frac{1}{2}},$$

whereas a pseudo-spin glass can be approximated by

$$P(x) = \frac{1}{x(x-2)}.$$

Both probability functions lead to inhomogeneous systems that will, only after very long times, equilibrate. Thermodynamic equilibrium might not be attainable under laboratory conditions. Natural material, on the other hand, could equilibrate and it is uncertain how far laboratory experiments under largely inhomogeneous temperature and pressure conditions can be paralleled with the large-scale behaviour of the lower mantle.

Electronic transport properties

The tendency of the perovskite structure to distort locally also leads to the formation of polaronic states, because charge carriers interact sufficiently strongly with the surrounding lattice that their mobility is reduced and self-trapping is obtained. The relaxation time for the self-trapping mechanism is in the same order of magnitude as phonon times. Experiments on a shorter timescale, like XPS (X-ray photoelectron spectroscopy) 'see' a static picture of the polaronic particle and detect exotic valence states. Typical behaviour is encountered in WO_3 and structural derivatives containing transition metals such as Mo, Nb, V, Te and Ti. Gehlig *et al.* (1983) and Salje *et al.* (1979) have shown that W^{5+} is the typical ground state in the perovskite lattice including the stabilization due to phonon condensation. Anderson argued (in 1975) that the double occupancy of gap states can be more favourable energetically than in the case of separated electrons, if the electron repulsion is over-compensated by the joint lattice distortion due to both electrons. Consequently, this pair state has been called a bipolaron. Not until 1980 did Schirmer & Salje find conduction bipolarons in low-temperature crystalline WO_{3-x}. These bipolaron states can be dissociated via a photo effect with a maximum efficiency near 1.1 eV, the transport activation energy is 0.18 eV, which is typical for most perovskite structures containing transition metals.

An interesting question arises if we consider perovskite structures with a high carrier concentration. Iguchi *et al.* (1981) predicted theoretically that there exists a maximum carrier density that occurs, preventing any considerable overlap of the polaronic wave functions. If more carriers compete for the same lattice distortion, the surplus carriers have to populate the valence band. This behaviour was found experimentally by Salje & Guttler (1984) in WO_{3-x} where the critical carrier concentration is *ca.* $3.5 \times 10^{21}\ \mathrm{cm}^{-3}$. Similar critical densities were also recently observed in structurally closely related $NbO_{2.5-x}$ (Ruscher *et al.* 1988*a*) with $n_c \approx 1.7 \times 10^{21}\ \mathrm{cm}^{-1}$ and W–Nb–O with $n_c \approx 6.10^{21}\ \mathrm{cm}^{-1}$ (Ruscher *et al.* 1988*b*). Structural disorder due to cation disorder on the octahedral site again leads to additional stabilization of the localized states. Electrical transport is then reduced and a Mott-type conductivity ($\ln \sigma \propto T^{\frac{1}{4}}$) is observed in contrast to thermally activated hopping conductivity. The electronic behaviour depends heavily therefore, on the structural state of the materials and varies dramatically if the material is not in thermodynamic equilibrium.

CONCLUSION

It has been shown that the capacity of the perovskite structure to relax locally under symmetry reduction is the origin for structural phase transitions. It is also the origin for sluggish kinetic behaviour, in particular if impurities play a major role. Possible 'impurities' can be electrons (or holes), which are surrounded by deformation clouds. The electrical conductivity is dramatically reduced by this effect. It is very likely that mantle material of the general composition (Mg, Fe)SiO_3 shows a similar behaviour in thermodynamic equilibrium although such equilibrium is difficult to obtain in laboratory experiments. Any prediction of the behaviour under mantle conditions depends sensitively on the knowledge of the exact chemical composition and the structural state. Here, the effect of Ca and Fe on $MgSiO_3$ is particularly important and might be relevant to our understanding of the nature of the D″ layer. It is also important to note that small changes of the oxygen fugacity can lead to major changes of the physical behaviour of perovskite.

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Discussion

M. F. OSMASTON (*The White Cottage, Woking, Surrey, U.K.*). Does Dr Salje think that the high electrical conductivity acquired by perovskite-structured minerals at high impurity concentrations could apply to the D″ layer at the base of the mantle? If so, not only would core–mantle electromagnetic coupling torque become potentially much more significant but the D″ layer might electromagnetically screen us from observing higher frequencies and spatial harmonics in the geomagnetic variation. In view of the importance of removing heat from the core, to sustain convection within it, I wonder what happens to the total thermal conductivity of such minerals under D″ conditions?

E. Salje. I would indeed expect higher electrical conductivity in the D″ layer compared with the mantle material at lower depth. This could also imply strong layering and appreciable gradients of the current densities. It would be very important to obtain experimental results on iron-bearing $MgSiO_3$ under well-defined oxygen fugacities to determine the actual specific conductivities of these materials under mantle conditions.

There is no experimental evidence concerning the thermal conductivity at very high temperatures. As a general rule, we might assume that a high carrier concentration *increases* thermal conductivity. This effect could be compensated, or even over-compensated, by the *decrease* of thermal conductivity due to high defect densities. Iso-spin glasses show often dramatically low thermal conductivity at lower temperatures. It is not clear, however, how to extrapolate these data to higher temperatures and pressures.