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Elastic softening of leucite and the lack of polar domain boundaries†

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Abstract

Elastic properties of leucite have been investigated using resonant ultrasound spectroscopy over a temperature range from 300 to 1400 K. According to these measurements, elastic moduli soften by ~50% at the *Ia*3*d*-*I*4$_1$/*acd* ferroelastic transition temperature T_{c1} = 940 K relative to the value at 1400 K. A second softening is observed at T_{c2} = 920 K, corresponding to the structural change from the space group *I*4$_1$/*acd* to *I*4$_1$/*a*. These elastic anomalies are analyzed in a simple model under the assumption that the transitions observed at T_{c1} and T_{c2} can be approximated by a single pseudoproper ferroelastic transition. The two phase transitions are accompanied by a single peak in mechanical damping attributed to the high mobility of twin walls in the intermediate phase followed by pinning in the low-temperature phase. To determine whether twin walls in tetragonal leucite are polar, resonant piezoelectric spectroscopy and second harmonic generation measurements were performed, but no evidence of polarity was found.

Keywords: Pseudoproper ferroelastic transition, resonant ultrasound spectroscopy, domain wall pinning, domain wall mobility, resonant piezoelectric spectroscopy

Introduction

The mineral leucite ($KAlSi_2O_6$) undergoes two structural transitions at T_{c1} = 938 K and T_{c2} = 918 K (Grögel et al. 1984; Lange et al. 1986; Palmer et al. 1988, 1990). A ferroelastic transition occurs at T_{c1} from a cubic phase with the space group *Ia*3*d* to a tetragonal phase with the space group *I*4$_1$/*acd* (point group 4/*mmm*). The transition is continuous (second order) and entails the formation of ferroelastic twin pattern. In the cubic phase, diffuse tetragonal diffraction signals persist up to >1060 K (Palmer and Salje 1990; Palmer et al. 1989). The microstructure in this case is likely to correspond to tweed, which is comprised of orthogonal modulations that appear as cross-hatched patterns in electron diffraction (Putnis and Salje 1994; Bratkovsky et al. 1994). In the *I*4$_1$/*acd* phase the main twin orientation corresponds to lamellar twins parallel to the pseudo-cubic (101) planes. At T_{c2} leucite undergoes a second transition to a tetragonal phase with the space group symmetry *I*4$_1$/*a* (point group 4/*m*). The associated microstructure consists of merohedric twins that cross-cut lamellar twins. In both phases, the twin density is quite high. In particular, some leucite crystals, including those from the Leucite Hill, have one of the highest twin densities among minerals (Palmer et al. 1988, 1989). The rich microstructure formation in leucite has been studied extensively. Microstructures, especially ferroelastic twins, can give valuable information about the order parameters and spontaneous strains associated with a phase transition, as has been elucidated by Palmer et al. (1989, 1990) and Hatch et al. (1990). This information is often used to reconstruct the geological history of a mineral.

In this study, we focused on another aspect. It has been argued that materials that contain complex microstructures, may have "functional" properties inside twin walls (and other ferroic domain boundaries) and their precusors, such as tweed microstructure, even when these properties do not exist in the bulk (Wada et al. 2006; Salje and Zhang 2009; Salje 2010, 2012; Catalan et al. 2012; Aktas 2013a). Evidence for (super-)conducting domain walls, for example, has been obtained in $WO_{3-\delta}$ and $BiFeO_3$ (Aird et al. 1998; Aird and Salje 1998, 2000; Seidel et al. 2009, 2010). Polar character (ferroelectric, piezoelectric, ferrielectric, or flexoelectric) for twin walls has only recently been identified in perovskites $CaTiO_3$ and $SrTiO_3$ (Van Aert et al. 2012; Scott et al. 2012, 2013). As leucite has an extremely dense microstructure and shows dielectric anomalies at high temperatures (Palmer and Salje 1990), we were tempted to investigate whether polar properties were hidden inside these domain walls. We will show in this paper that microstructures and the phase transitions in leucite do indeed cause elastic softening but none of the domain walls show any sign of polarity.

Experimental methods

The sample used in this study was natural leucite from Italy and purchased from the Genuine Gemstone Company Ltd., U.K. Initially the sample had the shape of a triangular prism but it was ground to a thickness of 340 μm along the c axis to apply a higher electric field for the investigation of polar properties using RPS. The sample surfaces perpendicular to the c axis had an irregular shape and were approximately 20 mm² in area. These surfaces were covered with a thin layer of silver paste for RPS measurements.

For the investigation of high-temperature elastic properties, RUS measurements were performed in a heating sequence using a horizontal resistance furnace and the sample held lightly between the tips of alumina buffer rods (Migliori and Sarrao 1997; McKnight et al. 2008). Data were collected in a heating sequence (with ~30 K steps between 300 and 815 K, in 5 K steps between 815 and 895 K, in 2 K steps between 896 and 1002 K, in 5 K steps between 1010 and 1080 K, and

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in 20 K steps between 1090 and 1390 K. Elastic resonances were excited mechanically by applying 10 V across a piezoelectric transducer glued to the end of one of the buffer rods outside the furnace. A second transducer attached to the end of the other rod outside the furnace served as a detector. Each spectrum contained 50 000 data points over a frequency range from 150 to 1200 kHz. A 20 min settle time was allowed for thermal equilibration prior to the collection of each spectrum.

RUS data were analyzed using the software package IGOR PRO (Wavementrics). The peak frequency, f, and full-width at half maximum, Δf, associated with each mechanical resonance mode were determined by a fit of the data to an asymmetric Lorentzian function.

To detect possible polar correlations in the ferroelastic twin walls of leucite we used resonant piezoelectric spectroscopy (RPS) (Salje et al. 2013), which is the electrical analog of RUS. Instead of using a piezoelectric transducer, as in the case of RUS, elastic resonances of a sample are excited by the application of an alternating electric field across the sample. RPS signals are observed if the sample is locally or macroscopically piezoelectric. This means that even weak local polar correlations in twin walls (Salje et al. 2013) or other nanoscale microstructures, such as tweed, (Aktas et al. 2013) can be detected.

After RUS measurements, the sample was cooled down to room temperature, and RPS spectra were collected in a heating sequence between 300 and 1000 K with 50 K steps, except for the intermediate phase (between 920 and 940 K) where two spectra were collected. For these measurements, 20 V was applied across the large surfaces of the sample to collect 50 000 data points in the same frequency range as in RUS measurements.

Second harmonic generation (SHG) measurements were also performed on leucite (Fiebig et al. 2005). In SHG, two photons with the same frequency generate a photon with twice the frequency in a nonlinear medium. This phenomenon only occurs in the absence of spatial inversion symmetry. Therefore SHG microscopy and spectroscopy have been a common technique to investigate polar properties of materials both at macro- and micro-scales (Fiebig et al. 2005; Pugachev et al. 2012; Yokota et al. 2014). For the measurements on leucite, the wavelength of the incident beam was varied to scan both the vicinity of the optical band gap of leucite (~300 nm) and the infrared regime (600–1200 nm) for SHG response.

Results and discussion

RUS spectra of leucite between 290 and 1400 K are shown in Figure 1. Two characteristic temperature dependencies can be seen. Resonance peaks that shift slightly to higher frequencies with decreasing temperature are due to the alumina buffer rods and do not represent the elastic properties of leucite. Resonance peaks related to the phase transitions in leucite show peak frequencies that decrease as the temperature is reduced to the cubic-to-tetragonal transition at T_{c1} = 940 K. The spectra collected at T_{c1} = 940 K and that for T_{c2} = 920 K are shown in dark gray.

In Figure 2, the squared frequencies (large, filled circles) of two low-frequency modes (between 150 and 300 kHz) are plotted as a function of temperature. The squared frequency of a resonance is proportional to the elastic modulus associated with that mode (Migliori and Sarrao 1997). Thus, the dips observed in the temperature evolution of squared frequencies indicate a 50% softening of the effective elastic moduli at T_{c1} relative to values obtained at 1400 K. As seen in the inset of Figure 1, slight stiffening below T_{c1} is followed by further softening down to T_{c2} = 920 K, indicated by arrows.

The structural phase transitions in leucite are clearly identified by their respective mechanical softening of the elastic moduli. The observed softening is accompanied by elastic damping Q^{-1}, given by $\Delta f/f$. These data, plotted in Figure 2 (open circles), correspond to the same resonances whose frequencies are shown in Figure 2. In the cubic phase, Q^{-1} is small but gradually increases with cooling, and a large damping occurs in the intermediate phase stable between T_{c1} and T_{c2}. The singularity in Q^{-1} that occurs in the intermediate tetragonal phase cannot be related to the coexistence of phases as both phase transitions are continuous with no evidence of first-order character or coexistence of phases. The singularity in Q^{-1}, however, is most likely to due to highly mobile twin walls in the intermediate phase. The second damping effect relates to the slightly higher damping of the low-temperature phase compared with the cubic phase. This indicates that some domain walls (and possibly defects) can be moved by the applied stress (Walsh et al. 2006) although the effect is too small to be indicative for the collective movement of large numbers of twin wall in the tetragonal phase. We conclude that twin walls, which are highly mobile in the intermediate phase, become pinned in the low-temperature phase. The temperature

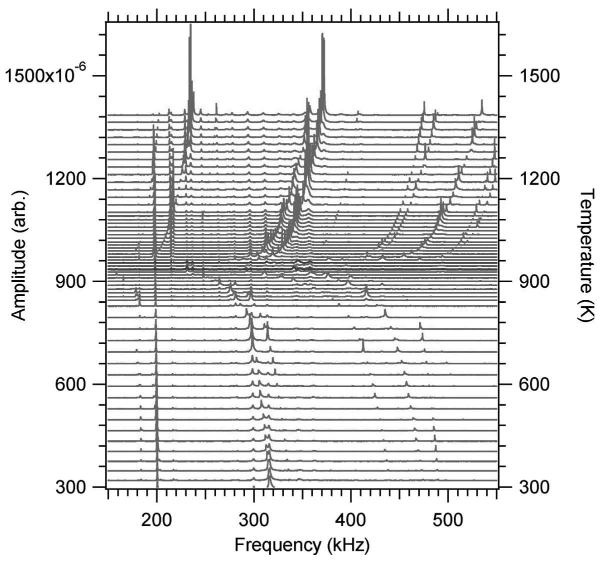

Figure 1. Resonant ultrasound spectra of leucite collected between 300 and 1400 K. Spectra were offset in proportion to the temperature at which they were collected and the right axis was labeled as temperature. Spectra shown in dark gray were collected at the *Ia*3*d*-*I*4$_1$/*acd* and *I*4$_1$/*acd*-*I*4$_1$/*a* transition temperatures T_{c1} = 940 K and T_{c2} = 920 K.

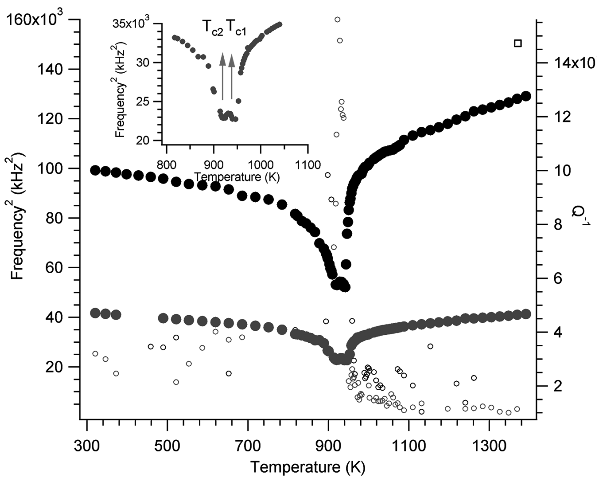

Figure 2. Temperature evolution of the squared frequencies (large, solid circles) of and mechanical damping (small, open circles) of two elastic resonances.

evolution of mechanical damping is analogous to the behavior of *I*4/*mcm* and *Pnma* perovskites. The former have highly mobile twin walls and one order parameter and the latter have immobile twin walls and two order parameters (Carpenter and Zhang 2011; Salje et al. 2013; Scott et al. 2012).

To determine whether domain walls in RPS are polar, RPS measurements were also performed. However, we did not find any elastic resonance signal so that no polarity is visible in leucite. This indicates either that the polarity is too weak to be seen in RPS or that the dipole moments cannot be switched in weak electric fields. The first interpretation is similar to microstructures in fully isotropic glasses where no RPS signals are seen. The second scenario is observed in $CaTiO_3$ where the twin boundaries are polar, as seen by transmission electron microscopy (Van Aert et al. 2012), but RPS signals are extremely weak (which will be published elsewhere). In leucite the domain walls are heavily pinned, and no polar switching occurs in the twin wall. To further investigate whether twin walls have polar character SHG measurements were also performed but no evidence of polarity has been observed. The SHG measurements thus confirm that if domain walls in leucite are polar, the polarity is too weak to be detected and much higher pulse and photon energies would be needed.

The elastic softening observed with RUS compares to that measured by dynamical mechanical analysis, which indicates the absence of significant frequency dispersion and domain wall related softening of elastic properties (Walsh et al. 2006). The elastic collapse observed with both techniques is one of the largest seen in any mineral and deserves a little more elaboration. One possible mechanism is the direct coupling of the ferroelastic strain with the structural order parameter (Boysen 1990; Heaney and Veblen 1990; Palmer 1990; Palmer et al. 1989, 1990; Carpenter et al. 1998). Such phase transitions are classified as pseudoproper ferroelastic transitions (Carpenter and Salje 1998) and their temperature evolution of a specific elastic modulus is predicted to follow

$$C = C_0 \frac{T - T_c}{T - T_o} \quad (1)$$

where C_0 is the value of the modulus at high temperatures, T_c is the critical temperatures renormalized as a result of the coupling between the order parameter and asymmetry-breaking strain, and T_o is the transition temperature in the absence of coupling. For a cubic-tetragonal transition the relevant shear elastic constant is $(C_{11} - C_{12})$ and it has been assumed that the resonance peak near 320 kHz at room temperature is determined predominantly by this. Equation 1 describes a nonlinear temperature dependence of f^2 for with $T_c = 931.5$ K and $T_o = 949$ K for $T < T_c$, and $T_o = 916$ K for $T > T_c$. As shown in Figure 3, this simple model is surprisingly close to the experimental data. The additional modifications are twofold: first the split into two transitions leads to additional softening in the low-temperature phase, which is obvious from the data (Fig. 3). The more fundamental change concerns the cubic high-temperature phase. A uniform structure is expected to follow the model prediction very strictly as observed in other materials (Salje 1993). The observed additional softening of the elastic modulus relative to the model prediction is likely to

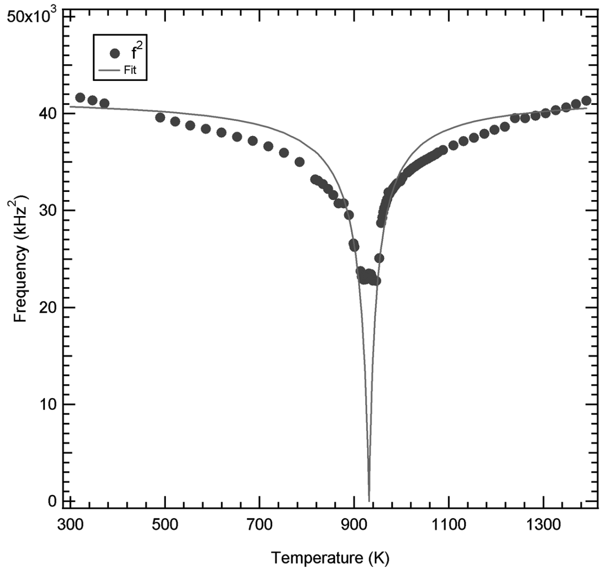

FIGURE 3. Comparison of the experimental data (circles) with a simple theoretical curve (continuous line) that combines the two transitions into one pseudoproper ferroelastic transition.

indicate that the phase is not uniform. Taking into account the increasing damping as the temperature is reduced to T_{c1}, the additional softening can be attributed to dynamic tweed microstructure (Putnis and Salje 1994; Bratkovsky et al. 1994). In the case of $PbSc_{0.5}Ta_{0.5}O_3$, for example, 25% softening of the shear modulus is attributed to such microstructure with a temperature dependence following the Vogel-Fulcher relationship (Aktas et al. 2013). The existence of tweed is consistent with the observation of X-ray reflections with tetragonal symmetry (Palmer et al. 1989) and birifrengence (Palmer et al. 1990) observed in the cubic phase. Moreover, DMA measurements performed at ~10 Hz also support this possibility (Walsh et al. 2006).

IMPLICATIONS

The elastic moduli of leucite are reduced by 50% at the *Ia*3*d*-*I*4$_1$/*acd* structural transition. These results show no significant frequency dispersion of elastic properties when compared to those obtained using DMA measurements, which found similar softening of the elastic moduli (Walsh et al. 2006). The characteristic signatures of microstructures are also evident in the elastic properties. In particular, twin walls become highly mobile in the intermediate tetragonal *I*4$_1$/*acd* phase and then get pinned in the room-temperature *I*4$_1$/*a* phase. Although this work does not provide any evidence of polar character in the twin walls, we hope that our work encourages further research to possibly discover such behavior in other minerals. With the recent discoveries of domain boundaries with functional (polar, magnetic, piezoelectric, conducting) properties in minerals and man-made compounds, a new research field, domain boundary engineering, has recently emerged to enable the fabrication of miniature devices using domain boundaries as active elements (Salje and Zhang 2009; Catalan et al. 2012; Salje 2010, 2012). Ideal examples are minerals with very dense domain boundary patterns and where the domain walls are thin (0.5–10 nm), which would naturally make them ideal nanoscale microstructures for many applications. Leucite would have been such an example although the domain walls appear to be non-polar, which rules out any piezoelectric or ferroelectric application. With that being said, readers are strongly encouraged to investigate other minerals, many of which are ferroelastic and may have such functional twin walls. RPS, for example, can be a good start for this investigation as it is very simple to implement (Salje et al. 2013; Aktas et al. 2013), and more detailed characterization of domain boundaries can be made with readily available nanocharacterization techniques.

Acknowledgments

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