On the elastic constants of the zeolite chlorosodalite

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Zeo...silicates, both naturally occurring minerals and synthetic materials, with widespread applications in catalysis, separation science, and ion exchange. Their atomic-scale structures, constructed from corner-shared tetrahedral silicate and aluminate units which encapsulate exchangeable cations and water molecules, have been the focus of study for a good many years because of these considerable practical uses. Recently several groups have begun to investigate the elastic properties of zeolite structures using various computational methods. One of these studies has predicted rather unusual properties: for example, by considering siliceous forms of zeolites (i.e., polymorphs of SiO2), it has been proposed that many zeolite frameworks should possess negative Poisson’s ratios, implying a counterintuitive lateral widening upon application of longitudinal stress in certain directions.

In order to verify the predicted elastic properties of zeolites, it is important to have access to experimental data concerning elasticity. Such data would also provide an important means of validation of the force fields used in performing simulations of the solid state. Of the numerous zeolites now known, however, the only three zeolites for which single-crystal elastic constants have been measured are chlorosodalite, Na8(Al2Si4O12)Cl2,5 natrolite, Na2(Al2Si3O10)·2H2O,6,7 and analcime, Na10(Al16Si32O96)·16H2O.8 Elastic constants have also been reported for a related material, dodecasil-3C, a silica clathrate which contained guest molecules, but in general there is a dearth of elastic data for these open-framework silicate structures. Here we report molecular simulation data which strongly suggest that in one of these previous reports an error exists in the published elastic constants of the material. When the previous experimental data are corrected by transposing the published directional ultrasound velocities, excellent agreement is observed between the off-axis plots of sodalite produced by experiment and modeling. Further confirmation of the prediction is supplied by considering the Zener ratios of other inorganic materials that possess cubic symmetry. © 2006 American Institute of Physics. [DOI: 10.1063/1.2162859]

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The use of force-field based molecular modeling to predict the elastic constants of the zeolite chlorosodalite is described. Theoretical predictions of the on-axis and off-axis elastic constants strongly suggest that an error exists in the published elastic constants of the material. When the previous experimental data are corrected by transposing the published directional ultrasound velocities, excellent agreement is observed between the off-axis plots of sodalite produced by experiment and modeling. Further confirmation of the prediction is supplied by considering the Zener ratios of other inorganic materials that possess cubic symmetry. © 2006 American Institute of Physics.
$E_y/E_z$ at this rotation. A similar trend is observed for the Poisson’s ratios: $\nu_{xy}$ is at a minimum and $\nu_{yz}$ is at a maximum at $45^\circ$ to the axis for the modeled data while for the published elastic constants, $\nu_{xy}$ is at a maximum and $\nu_{yz}$ is at a minimum at this rotation. In order to correct this disagreement, the reported sound velocities which were measured for the $x$ and $y$ crystal directions simply need to be swapped. The form of the off-axis plots, Fig. 1, then shows excellent agreement with the experimental data. This suggests an error in either manipulation of the single crystal specimen, or in reporting the experimental data, in the original publication.

A convenient way of quantifying the degree of off-axis anisotropy in the elastic constants for a cubic crystal is to use the Zener ratio $Z = 2 \cdot \frac{C_{44}}{C_{11} - C_{12}}$. The elastic constants of a number of materials with cubic crystal symmetry have been reported and it may be observed that the Zener ratio takes a wide range of values, from 0.4 for KCl to 2.4 for MgAl$_2$O$_4$, for example. Those materials with closely related atomic compositions and structures, however, exhibit similar Zener ratios: for example, the rock-salt oxides MnO and CoO have Zener ratios of 1.41 and 1.43, respectively, while for the ternary, spinel-type oxides Fe$_2$O$_4$ and FeCr$_2$O$_4$, the values of 1.12 and 1.32, respectively, are found. This is not surprising as the elastic constants depend on the crystal structure and interatomic forces. Analcime is the only other cubic aluminium silicate zeolite for which elastic constants have been measured, and this has a Zener ratio of 0.71, close to the predicted Zener ratio of 0.74 for chlorosodalite. By comparison, the Zener ratio calculated from the original experimental data for chlorosodalite is 1.46 whereas the Zener ratio using the corrected experimental data is 0.72. Figure 2 shows off-axis plots of Young’s moduli and Poisson’s ratios of analcime, spinel, MgAl$_2$O$_4$, and potassium chloride, KCl. This demonstrates the sensitivity of these plots to the chemical nature, and hence, atomic structure, of the material studied, and therefore how these data must also be used as a test of any simulated elastic data, in addition to the on-axis values of elastic constants. The similarity of the polar plot for analcime and the corrected plot for chlorosodalite, further backs our conclusion that the published elastic constants for chlorosodalite are incorrect due to transposition of experimental data.

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FIG. 2. Off-axis plots produced by rotation about the x axis for the Young’s moduli and Poisson’s ratios of the cubic materials potassium chloride, KCl, analcime, Na₁₆Al₁₆Si₃₂O₉₆·1₆H₂O, and spinel, MgAl₂O₄. The value of Zener ratio, Z, is quoted for each material.