

Temperature insensitive negative Poisson's ratios in isotropic alloys near a morphotropic phase boundary

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Poisson's ratio, shear modulus, and damping of polycrystalline indium-tin (In-Sn) alloys in the vicinity of the morphotropic γ - $\gamma + \beta$ phase boundary were measured with resonant ultrasound spectroscopy. Negative Poisson's ratios were observed from 24 °C to 67 °C for alloys near the phase boundary. Properties were unaffected by annealing at 100 °C for 2 days. This isotropic fully dense negative Poisson's ratio material is temperature insensitive, in contrast to other materials that undergo phase transformation. © 2012 American Institute of Physics.

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Poisson's ratio (ν), defined as the ratio of lateral to longitudinal strain during longitudinal stretch, reveals the relative tendency of a material to undergo shape or volume change when subjected to mechanical loading. The range for Poisson's ratio is $-1 < \nu < 0.5$ for isotropic materials, but most common materials exist within the narrower¹ range of $0.25 < \nu < 0.35$. Foam materials with cells of re-entrant shape have been made with Poisson's ratio as small as -0.7 .² Void space is not necessary to obtain negative Poisson's ratio; hierarchical laminates with high contrast between phases can exhibit such effects.³

As for nonporous (fully dense) materials, negative Poisson's ratios have been inferred for certain directions in *anisotropic* single crystals such as pyrite,⁴ α -cristobalite, and cubic metals (and some hexagonal crystals) stretched along the [110] direction.⁵ However, the inference for pyrite has been disputed⁶ based on further ultrasonic results. A negative Poisson's ratio was found during large tensile deformation along a specific direction of the nacre from *Hyriopsis schlegeli* shells.⁷ For carbon nanotubes, Poisson's ratio becomes small but still positive as the chirality increases.⁸ In highly oriented nanotube structures, negative Poisson's ratio (auxetic behavior) has been reported^{9,10} based on orientation of the tubes. Anisotropic solids exhibit effects such as stretch-twist coupling, so negative Poisson's ratio is not so counterintuitive in such solids. Polycrystalline *isotropic* materials almost always display positive Poisson's ratios due to the averaging of effects in different directions. However, calculations based on single crystal α -cristobalite¹¹ indicate the polycrystalline solid may possess a negative Poisson's ratio, though experiment has not been done.

In nonporous *isotropic* materials, negative Poisson's ratios have been inferred from the measured elastic constant softening over a narrow temperature range in the vicinity of displacive phase transitions. For example, negative Poisson's ratios were inferred from the measured softening in the shear and bulk moduli of polycrystalline barium titanate (BaTiO_3) during the cubic to tetragonal phase transformation^{12,13} near 120 °C. Similarly for polycrystalline quartz (SiO_2), negative Poisson's ratios were inferred from elastic constant softening

during the α - β phase transformation¹⁴ near 573 °C. In a polymer gel near a volumetric phase transformation near 33.8 °C, negative Poisson's ratio was also observed.¹⁵ For the polycrystalline ceramics, softening of the effective shear modulus was relatively modest; the minimum in Poisson's ratio was associated with the softening of the bulk modulus within a narrow temperature range. In these materials, the negative Poisson's ratio effect is highly temperature sensitive. Negative Poisson's ratio nonporous materials that are *insensitive* to temperature have not been reported.

Negative Poisson's ratio in nonporous *isotropic* materials is of interest but as yet not observed over a wide temperature range. To that end, we consider elastic constants as a *function of composition*, rather than temperature. In that vein,¹⁶ experiments on indium-tin (In-Sn) alloys between 0 and 30 wt. % In disclosed a minimum ν of +0.125 for 10.5 wt. % In. The minimum in ν was attributed to proximity to the $\beta\text{Sn} + \gamma$ - γ phase boundary. However, since the compositional increments were on the order of 3 wt. % In, the resolution was not sufficient to adequately probe the minimum. The $\beta\text{Sn} + \gamma$ - γ phase boundary is of particular interest in that it is a *morphotropic* phase boundary, which is nearly vertical in the vicinity of ambient temperature. Morphotropic phase boundaries are of more general interest, particularly in the context of high performance piezoelectric materials such as lead titanate zirconate.¹⁷ Compositions near the morphotropic phase boundary may have two phases that coexist over a range of temperature. In piezoelectric ceramics, this entails a large number of polarization directions that are established during the poling process, giving rise to high piezoelectric and dielectric properties.¹⁸ In this letter, we report negative Poisson's ratios for fully dense polycrystalline metal alloys near a morphotropic phase boundary over a range of temperature.

Samples were made by casting tin shot (Alfa Aesar, 99.99 + %) and indium pieces (cut from an indium rod, Alfa Aesar, 99.999%) inside vacuum sealed glass tubes to obtain compositions between 8 and 20 wt. % In and also 100% In. Crucibles were heated to 330 °C; after melting, the molten metal was mixed by upending the crucible several times until

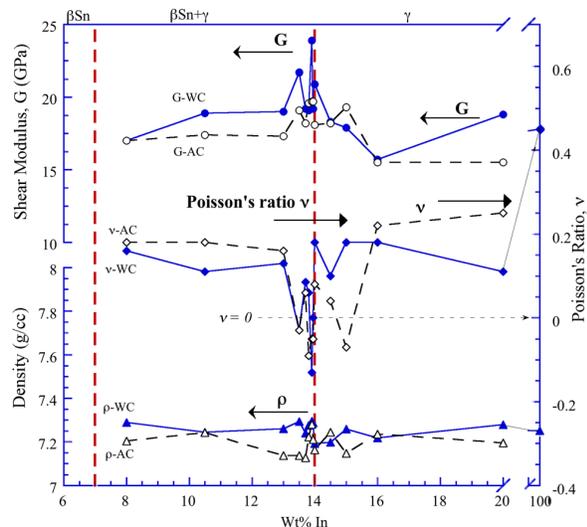


FIG. 1. Density (ρ), shear modulus (G), and Poisson's ratio (ν) of the as-cast In-Sn alloys at ambient temperature as a function of wt. % In and cooling rate. WC indicates water cooled (solid symbols); AC indicates air cooled (open symbols). Measurements of ρ and ν for pure In are also shown for comparison. G for pure indium was about 4 GPa (not shown).

the metal solidified. The crucible was reheated and the melt-remelt process was repeated five times. For the final solidification, sample tubes were either allowed to air cool (AC) in a vertical position or were dropped into a beaker of room temperature water (WC). A water cooled and an air cooled sample was made for each composition. Samples, cylinders of length equal to diameter (to facilitate interpretation of resonant modes), were sectioned using an abrasive diamond saw. The ends were polished flat and perpendicular to the cylinder axis. Sample densities were measured using an Archimedeal immersion technique. Shear modulus, Poisson's ratio, and damping were measured via resonant ultrasound spectroscopy (RUS) using the method of Jaglinski and Lakes.¹⁹ The fundamental torsion mode and the bending modes were identified through use of shear polarization sensitivity. Poisson's ratio was determined by aligning the observed mode structure from the first few modes with the Demarest plot over the full range of isotropic Poisson's ratio. This graphical method is insensitive to slight imperfections in the sample (heterogeneity, slight anisotropy) because the first few modes suffice to determine the isotropic elastic constants. Damping ($\tan \delta$) was determined via measurements of the width at half maximum of the appropriate resonant peak. For split modes (as observed in bending), the damping of the

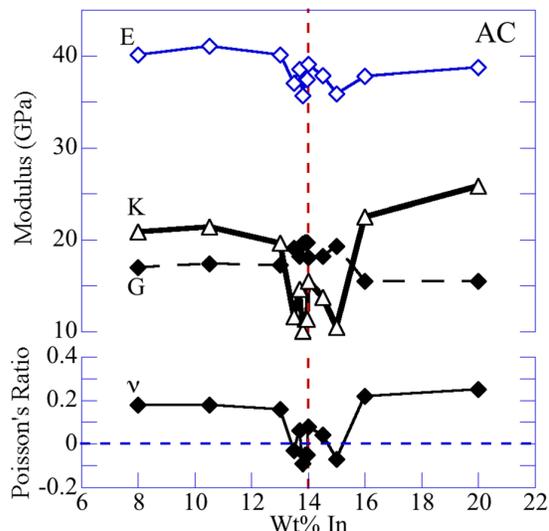


FIG. 3. Inferred Young's modulus (E) and bulk modulus (K) from the measured shear modulus (G) and Poisson's ratios ν of AC alloy. The vertical dashed line represents the nominal $\beta\text{Sn}+\gamma-\gamma$ phase boundary at room temperature.

first peak was measured. Heating of the sample in the RUS apparatus was accomplished by flowing hot air from a small resistance tube heater over the sample. Temperature was monitored by two thermocouples and the gradient maintained using an insulating blanket to less than 1°C across the sample. Temperature was increased in 4° steps and allowed to reach steady state. Total test time was about 4 h, for an average heating rate of $\sim 0.3^\circ\text{C}/\text{min}$. The upper limit on temperature was dictated by the commercial ultrasonic nondestructive test transducers used in the present method.

Figure 1 shows the shear moduli (G), Poisson's ratios (ν), and densities (ρ) of the as-cast samples over the full compositional range studied here. Pure indium exhibited $\nu = 0.45$, and $G = 4$ GPa, consistent with the literature. A minimum ν of -0.13 was obtained for water cooled 13.9 wt. % In-Sn; a minimum of -0.1 was obtained for air cooled 13.8 wt. % In-Sn. There were three closely spaced minima in Poisson's ratio in the vicinity of the $\beta\text{Sn}+\gamma-\gamma$ phase boundary according to the phase diagram²⁰ and shown as the vertical dashed line in Fig. 1. The shear modulus displayed a modest peak near the boundary; density exhibited no obvious sensitivity to the phase boundary. $\tan \delta$ for torsion was 1.3×10^{-3} and for bending $0.6\text{--}2.5 \times 10^{-3}$, with no obvious sensitivity to the phase boundary. As for repeatability, a

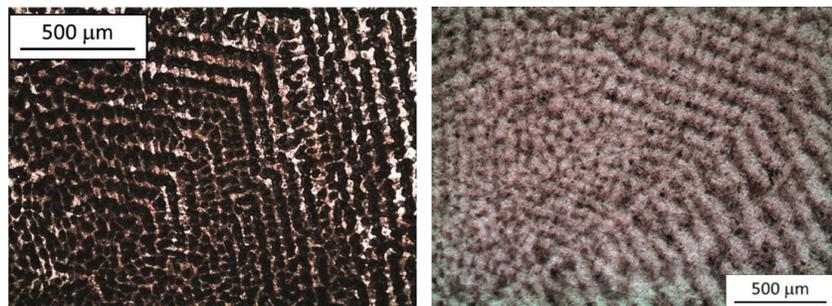


FIG. 2. Optical micrograph of air cooled InSn samples: Left, 15 wt. %, Right, 13.5%.

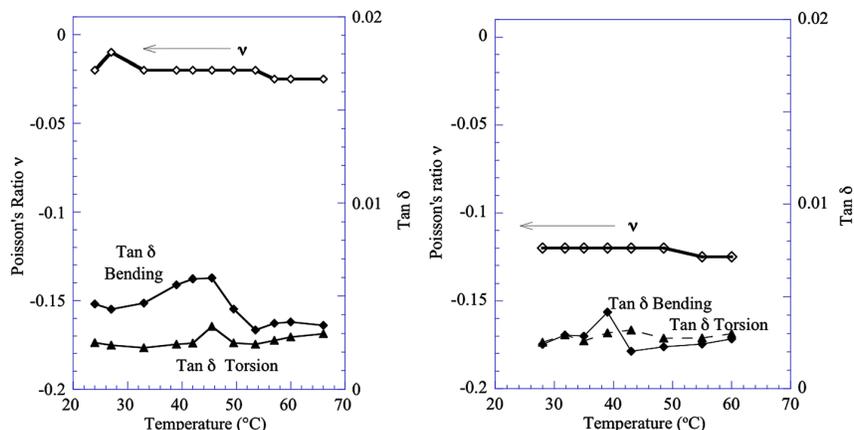


FIG. 4. Poisson's ratio (open diamonds) and $\tan \delta$ (torsion, solid triangles; bending, solid diamonds) vs. temperature for as-cast 13.5 wt. % (left) and 13.9% (right) In-Sn water cooled samples.

second casting for 15% wt. % In (AC) was made and tested with results almost identical to those shown in Fig. 1.

Optical microscopy of the as-cast samples revealed the microstructure of the samples (Fig. 2). The microstructure due to solidification was obviously dendritic. Dendrites were on the order of millimeters in size; their arm spacing depended on cooling rate such that air cooled samples had a spacing $40\ \mu\text{m}$ - $70\ \mu\text{m}$ and water cooled samples had a spacing $15\ \mu\text{m}$ - $25\ \mu\text{m}$. The microstructure bears some resemblance to the hierarchical laminate structure envisaged by Milton³ to exhibit negative Poisson's ratio. However, the Milton laminates require careful tuning of constituent properties and of sub-laminate geometry to achieve negative Poisson's ratio. Moreover, dendritic structures occur in both the positive Poisson's ratio compositions studied here and also in other materials. Therefore, we do not attribute the negative Poisson's ratio to micro-scale structure; the pertinent structure may be on a finer scale.

Inference of Young's Modulus E and bulk modulus K from the measured G and ν via the usual isotropic elasticity relations $E = 2G(1 + \nu)$ and $K = 2G(1 + \nu)/3(1 - 2\nu)$ shows that the bulk modulus softens considerably (Fig. 3) and the shear modulus G increases slightly near the phase boundary. By contrast, a slight softening of G was observed in BaTiO_3 .

The effect of temperature was evaluated from 24°C to 67°C for as-cast, water cooled 13.5, 13.7, 13.9, and 20 wt. % In-Sn. The effect of temperature was minimal: in all cases, G (not shown) and ν remained essentially constant over the temperature range (Fig. 4). Small damping peaks were observed for some compositions in torsion and bending as shown in Fig. 4 for 13.5 wt. % and 13.9 wt. % In-Sn. Damping in the vicinity of phase transformations is rate dependent. Therefore, small damping peaks at the slow rates used in this study may be due to minimal intrinsic damping associated with the transformation.

Several samples (13.5, 13.7, 13.9, and 15 wt. % In, all water cooled) were vacuum annealed for 2 days at 100°C , at least 25° below the eutectic temperature. No significant change in the mechanical properties occurred after annealing.

Effects of slight material heterogeneity were revealed in the resonance structure: higher modes were in some cases split or shifted; maximum splitting was less than 2%. This is perhaps not surprising in view of the dendritic structure observed. Moreover, despite efforts to achieve macroscopic

homogeneity, there was some heterogeneity in the cast ingots. For the 13.7 wt. % In ingot, two samples sectioned from the same ingot exhibited $\nu = 0.07$, and a third sample exhibited $\nu = 0.23$. Properties near the phase boundary are highly sensitive to composition. Indeed, compositions further from the phase boundary showed less variation.

As for phase transitions, softening of single crystal elastic constants (shear moduli) to near zero has been observed in a number of single crystals at the critical temperature.²¹ Polycrystalline metals²² and ceramics¹³ also display elastic constant softening, with sharp temperature dependence, during phase transitions. Morphotropic phase transitions, pertinent to high performance piezoelectric materials, are not fully understood in that context.²³ Too, they are not prominent in the mechanical property literature, though some analysis of softening of shear moduli has been done in the context of martensitic alloys.²⁴ It is likely that the present results have bearing on other morphotropic transitions.

In conclusion, negative Poisson's ratios for nonporous, polycrystalline alloys were obtained in association with the phase boundary near 14 wt. % In at and above room temperature. Specifically, minimum values for Poisson's ratio of -0.13 and -0.1 were obtained for water cooled 13.9 wt. % In and air cooled 13.8 wt. % In-Sn alloys, respectively. As-cast mechanical properties displayed little sensitivity to temperature increases of more than 40°C in the RUS apparatus or after annealing at 100°C for 2 days. Increased solidification rate resulted in slightly denser and stiffer samples. This isotropic fully dense negative Poisson's ratio material is temperature insensitive. Such a material is in contrast to other materials that undergo phase transformation.

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