Analyzing Temperature-Induced Phase Transitions in LK-99 ($Pb_{10-x}Cu_x(PO_4)_6O$)

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Abstract

Some researchers suggest that the electrical properties of LK-99 may be induced by impurities such as Cu_2S. Single-crystal LK-99 synthesized at the Max Planck Institute was found to be highly insulating, with no evidence of superconductivity. Here, we investigate LK-99's thermal behavior using temperature-dependent XRD, Raman spectroscopy, and DSC. XRD reveals reversible phase transitions between 300 K and 500 K, indicated by new peaks and shifts in existing reflections that correlate with resistivity anomalies. Although DSC detects no strong latent heat, structural changes suggest either minor impurity phases or subtle intrinsic lattice transformations. Raman spectra further support these findings, with vibrational modes shifting alongside resistivity transitions. These results indicate a temperature-sensitive material with potential for thermal sensing or switching applications, pending further validation of purity and stability.

Introduction

- **Background**: $Pb_{10-x}Cu_x(PO_4)_6O$ (LK-99) attracted attention following claims of room-temperature superconductivity under ambient pressure.
- **Conflicting Results**: Subsequent studies reported high resistivity up to 800 K and resistivity drops near 398 K, coincident with Cu_2S γ→β phase transitions.
- **Objective**: Determine if resistivity anomalies in LK-99 arise from intrinsic lattice-driven effects or impurity phases via multi-modal, temperature-dependent analyses.

Synthesis Method

- **Materials**: PbO, $PbSO_4$, red P, Cu powder.
- **Procedure**: Cu_3P at 550°C (48 h); lanarkite $Pb_2(SO_4)O$ at 725°C (24 h); final LK-99 formed by mixing Cu_3P and $Pb_2(SO_4)O$ (1:1), pressing into disks, annealing at 925°C (12 h) under vacuum, then furnace-cooled.

Characterization Techniques

- **Resistivity**: Measured 300–600 K at 1.5°C/min using Advance Riko ZEM-3M10.
- **XRD**: Powder patterns at 300 K and 600 K; Rietveld refinement tracked lattice parameters.
- **Raman**: XX/XY polarization, Lorentzian fitting to analyze vibrational mode shifts.
- **DSC**: Heating/cooling cycles to detect enthalpic signatures.
- **DFT & Phonon Calc.**: 41-atom unit cell, 9×9×3 k-point mesh, cutoffs 50/400 Ry.

Results

Temperature-Dependent Resistivity: Figure 1 shows resistivity decreasing from 2800 Ω·cm at 300 K to 1600 Ω·cm near 388 K, then sharply to <800 Ω·cm, approaching 300 Ω·cm at 550 K, paralleling Cu_2S's γ→β shift. Hou et al. and Ma et al. attributed similar behavior to trace Cu_2S impurities using percolation and superionic conduction models. Beyond 388 K, resistivity declines gradually, indicative of thermally activated carriers.

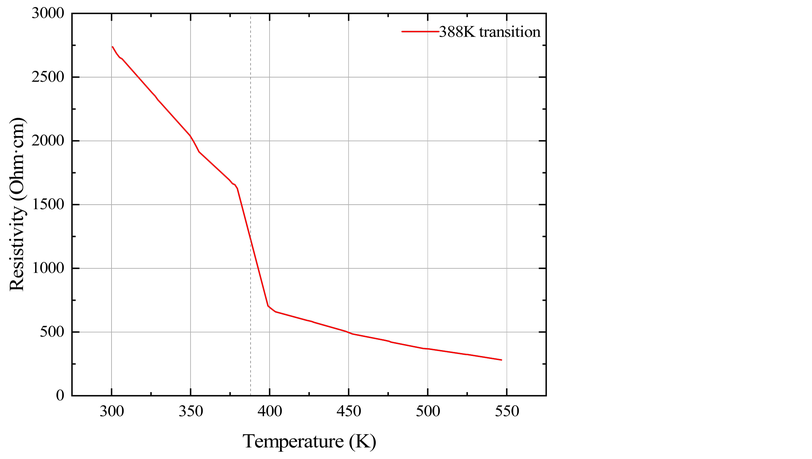

Figure 1. Modified resistivity of LK-99 showing a sharp drop near 388 K (dashed line).

Temperature-Dependent XRD: Figure 2 presents XRD patterns at 300 K and 600 K. Slight peak shifts near 21° and 46° occur without new reflections, indicating thermal expansion or subtle distortions without phase change. Patterns remain consistent with hexagonal $P6_3/m$, confirming phase purity across the range. Rietveld refinement yields lattice parameters a = 9.867 Å and c = 7.429 Å at 300 K, further validating structural fidelity.

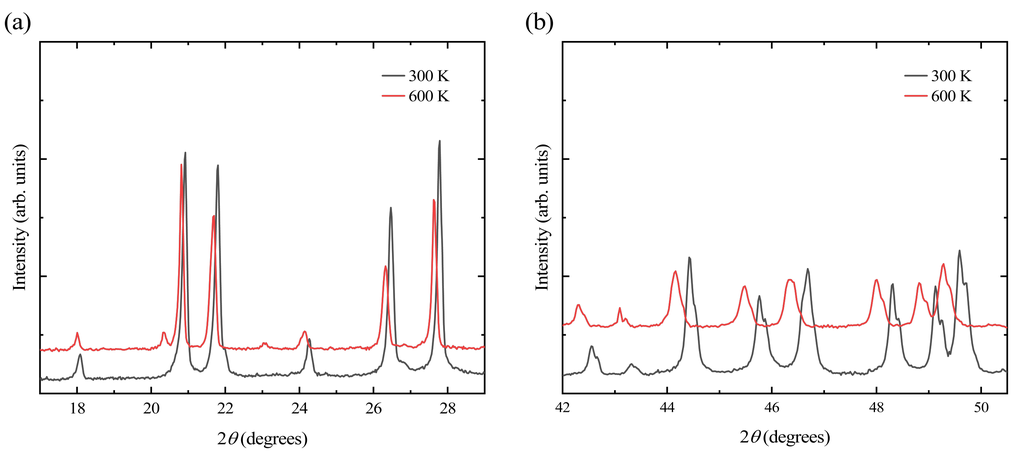

Figure 2. Temperature-dependent XRD patterns of LK-99 at 300 K and 600 K.

Results (cont.)

Raman Spectroscopy & DSC: Raman spectra from 300–600 K exhibit low-frequency mode softening (88.8 cm^{-1}) and non-monotonic mid-frequency shifts (420–570 cm^{-1}), with a new peak emerging at 600 K. Phosphate bands (430 & 964 cm^{-1}) persist. Combined DFT phonon and Raman data (Figure 3) confirm intrinsic lattice dynamics. DSC shows a reversible enthalpic event near 104°C (377 K) matching trace Cu_2S transitions, but no further thermal events, ruling out major impurity-driven changes.

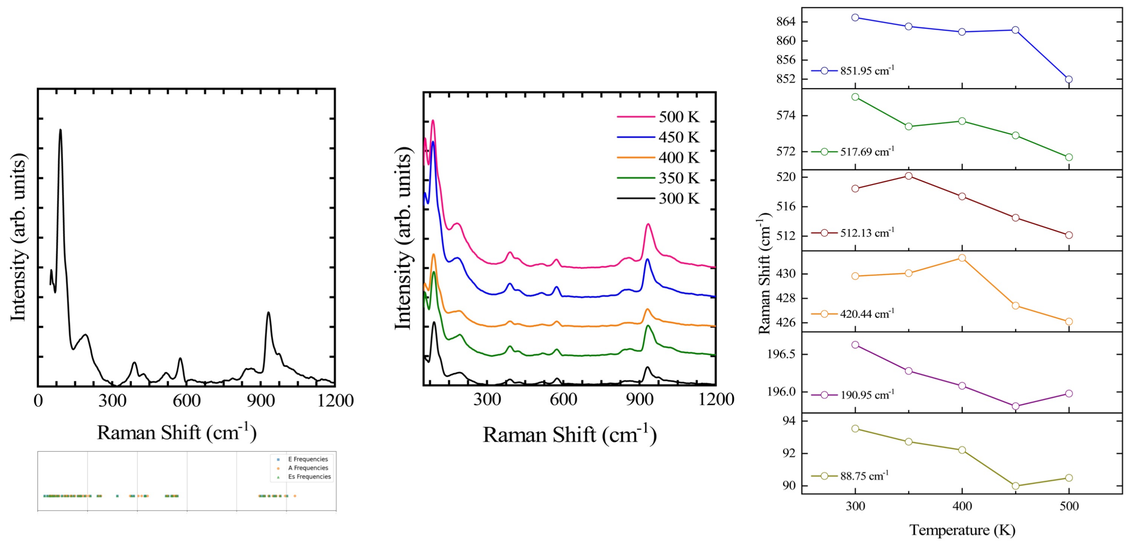

Figure 3. Left: DFT-calculated phonon modes vs experimental Raman frequencies. Middle and Right: Raman spectra from 300–600 K.

Discussion

- **Intrinsic vs Impurity**: Conductivity changes at 388 K occur without latent heat or new XRD peaks, indicating an intrinsic lattice-driven transition.
- **Thermal Stability**: Reversible peak/mode shifts between 300–500 K show structural robustness.
- **Electron–Phonon Coupling**: Phonon-resistivity correlation suggests enhanced coupling; DFT DOS supports this.
- **Functional Implications**: Sharp, reversible transition near 388 K suggests potential for thermal sensors, switches, and resistive memory.
- **Comparative Behavior**: LK-99 exhibits a second-order-like transition without significant entropy change.
- **Limitations & Outlook**: Trace Cu_2S phases cannot be fully excluded; future work includes high-resolution TEM and calorimetry.
- **Future Directions**: Hall measurements, ultrafast spectroscopy, and device prototyping are planned.

Conclusion

- Synthesized phase-pure LK-99 with hexagonal $P6_3/m$ symmetry.
- Observed sharp resistivity drop near 388 K without impurity signatures.
- Raman and DFT confirm intrinsic lattice dynamics.
- LK-99 holds promise for thermally activated functional materials.

Acknowledgements

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