

Raman scattering in mercury-based high- T_c superconducting ceramics

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Raman scattering spectra have been measured in superconducting samples of the mercury-cuprate homologous series $\text{HgBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2+x}$ with $n=1, 2, 3$. A comparative analysis of these results and the corresponding data on thallium-based high- T_c superconductors is carried out. All the observed Raman scattering lines (or frequencies) are attributed to combinations of O1 and O2 oxygen. The Raman scattering spectrum of a precursor of the 1212 phase, $\text{Ba}_2\text{CaCu}_2\text{O}_5$, has been studied.

It has not been long since the development of the mercury-based high- T_c superconductors (March of 1993). The first experiments were naturally aimed at synthesizing the family of layered cuprates $\text{HgBa}_2\text{R}_{n-1}\text{Cu}_n\text{O}_{2n+2+x}$, primarily the compositions with $n=1, 2, 3$, since it had been found that the transition temperature T_c of the 1223 composition reached saturation^{1,2} ($T_c=131-133$ K).

The mercury cuprates are ideal high- T_c superconductors, since they have an undeformed lattice, among several other advantages. Interest has naturally been attracted to an in-depth study of the Hg-1201, 1212, and 1223 phases, despite the fact that only powders and ceramics are available at this point.

Our measurements were carried out for 1212 and 1223 ceramics synthesized under pressure with the help of molybdenum cells at the Institute of High Pressure Physics, Russian Academy of Sciences,² and for a 1201 powder synthesized in quartz

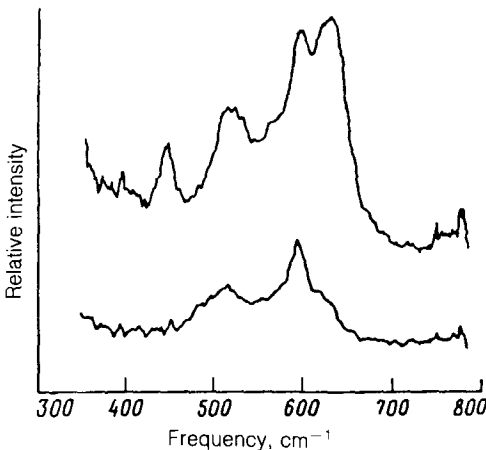


FIG. 1. Raman scattering spectra of an Hg-1212 sample at two different spots on the sample.

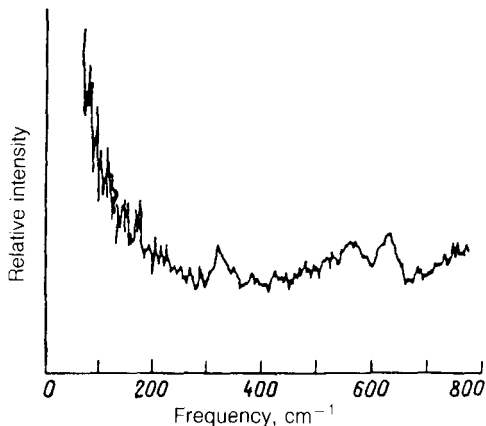


FIG. 2. Raman scattering spectrum of the precursor $\text{Ba}_2\text{CaCu}_2\text{O}_5$.

cells (without pressure) in the laboratory of E. V. Antipov at Moscow State University. After the synthesis, all samples were annealed at $T = 300^\circ\text{C}$ for about 10 h in an atmosphere of pure oxygen. Measurements of the susceptibility of the ceramic samples revealed that the 1223 samples consisted of two phases. The transition temperatures of the samples of all phases corresponded to the known results. The minimum transition width in our best samples was ~ 4 deg.

We studied the Raman scattering spectra of these samples. Where necessary, the powders were pressed into pellets to improve heat transfer. Raman spectra were excited by an argon laser at wavelengths of 514.5 and 488 nm at a power level of 1–10 mW (depending on the sample). The light was focused into a spot about $10\ \mu\text{m}$ in diameter. The spectra were recorded by a triple spectrograph with a multichannel recording system (which had been developed in a collaboration with the Institute of Spectroscopy, Russian Academy of Sciences). The resulting spectra depended on the

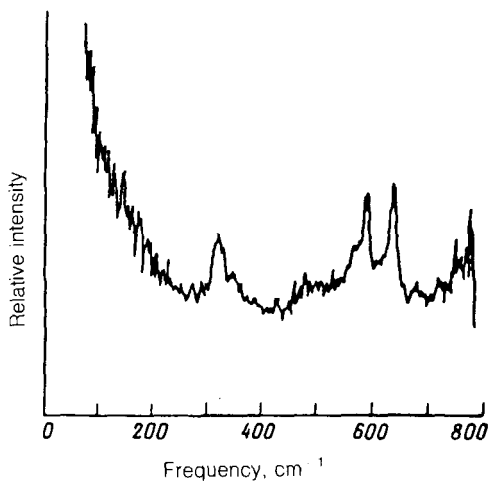


FIG. 3. Raman scattering spectrum of an Hg-1201 sample.

TABLE I. Identification of the vibrational frequencies in the Hg cuprates (all frequencies are in reciprocal centimeters).

Vibrational mode	Hg cuprate			Tl cuprate	
	1201	1212	1223	1212 (experimental ³)	1212 (theoretical ⁴)
02, A_{1g}	590	598	—	520	518
01, A_{1g}	—	516	510	406	438
01, $E_{g }$	637	628 ¹⁾	680	—	608
01, $E_{g\perp}$	—	447	—	—	421

^{*}The frequencies of the Raman lines of the precursor are 324, 563, and 631 cm^{-1} . These lines are also observed in the Hg-1201 and 1212 phases.

¹⁾The 628- cm^{-1} line in the 1212 sample is very intense; its proximity to the 631- cm^{-1} line of the precursor may be simply a matter of chance.

particular point selected on the sample; this result was not surprising since our method is actually a microprobe analysis method. In order to eliminate the influence of phases used in the course of the synthesis, we studied the Raman spectrum of a $\text{Ba}_2\text{CaCu}_2\text{O}_5$ powder, which is a precursor of the basic 1212 phase which we have studied.

Figure 1 shows spectra for the 1212 phase from two different points on one sample. Figure 2 shows spectra of the $\text{Ba}_2\text{CaCu}_2\text{O}_5$ precursor. Figure 3 shows spectra for a 1201 sample (a pressed pellet). The results are summarized in Table I.

We carried out a comparative analysis of our results with experiments on Raman scattering in thallium-based high- T_c superconductors with a corresponding structure and with corresponding selection rules for vibrational modes.³ We also compared our results with the calculations of Ref. 4. On the basis of these comparisons we have tentatively assigned vibrations to the frequencies which we observed (Table I). Also shown in Table I are frequencies corresponding to the precursor.

The higher vibration frequencies A_{1g} in the mercury cuprates do not contradict existing structural data (the lattice constant c in tetragonal structures in Tl cuprates is larger than in Hg cuprates).

We were unable to detect Raman scattering by low-frequency vibrational modes corresponding to vibrations of the heavy Ba and Cu atoms. In an effort to explain the Raman spectra we assumed that the E_g vibrations, which are not observed in Tl cuprates, are manifested in the Raman spectra of Hg cuprates. In identifying the E_g vibrations we worked from theoretical data⁴ on Tl cuprates. A more accurate identification of the vibrations will become possible when good ceramics and, especially, single crystals of the Hg-based high- T_c superconductors become available.

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⁴T. Mori *et al.*, Solid State Commun. **72**, 125 (1989).

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