

## Second optical harmonic in the ceramic $\text{La}_{1.8}\text{Sr}_{0.2}\text{CuO}_4$

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The second optical harmonic arises near the surface in the superconducting ceramic  $\text{La}_{1.8}\text{Sr}_{0.2}\text{CuO}_4$  during excitation by a copper-vapor laser. The corresponding optical nonlinearity is only an order of magnitude smaller than that of the typical ferroelectric barium titanate. It is concluded that at room temperature this ceramic contains clusters of a polar phase with a polarization direction perpendicular to the directions of metallization bonds.

The ceramic  $\text{La}_{1.8}\text{Sr}_{0.2}\text{CuO}_4$  has recently attracted considerable interest because of the discovery<sup>1,2</sup> that it undergoes a phase transition to a superconducting state. Such a ceramic is characterized by a structure which is similar to the perovskite structure.<sup>3,4</sup> A perovskite structure ( $O_h^1$  group) is observed in the high-temperature (paraelectric) phase of many ferroelectrics ( $\text{BaTiO}_3$ ,  $\text{KNbO}_3$ ,  $\text{PbTiO}_3$ ). As these crystals are cooled,

the displacement of sublattices lowers the point symmetry from cubic to tetrahedral, rhombohedral, or orthorhombic. In several cases the phase transition from the paraelectric phase to the asymmetric phase is accompanied by a loss of the inversion center in the structure, because the centers of gravity of the positive and negative ions in the unit cell do not coincide. Anomalies are observed in many properties near a transition of this sort. A distinctive feature of polar acentric structures is the appearance of rather large optical nonlinearities, in particular, a manifestation of a doubling of the frequency of exciting light: the second optical harmonic. In this letter we report a study of the possibility of observing the second optical harmonic in the ceramic  $\text{La}_{1.8}\text{Sr}_{0.2}\text{CuO}_4$  and a comparison of the magnitude of this effect with the corresponding values for the typical ferroelectric barium titanate.

The second optical harmonic is excited by a copper-vapor laser in pulsed operation, with output in the visible range ( $\lambda = 578.2 \text{ nm}$ ), with a fairly high average power ( $\geq 1 \text{ W}$ ), and with a fairly high peak power ( $\sim 10^4 \text{ W}$ ). The length of the output pulse is 20 ns at a repetition frequency of  $5 \cdot 10^4 \text{ Hz}$ .

Since this ceramic exhibits a metallic conductivity and is opaque to the exciting light, the second-harmonic signal can appear in it only in a thin surface layer, with a thickness less than  $0.1 \mu\text{m}$ . The experiments are accordingly carried out in a reflection arrangement, in which the second-harmonic signal ( $\lambda = 289.1 \text{ nm}$ ) is observed in reflected light, in a direction close to the specular reflection direction. The useful signal is detected at the exit from an MDR-2 spectrometer by an FEU-71 photomultiplier operating in a photon-counting mode. The average threshold sensitivity for the useful signal in the measurements system used<sup>6,7</sup> is  $\sim 10^{-14} \text{ W}$ , with a time constant  $\sim 1 \text{ s}$ .

The ceramic  $\text{La}_{1.8}\text{Sr}_{0.2}\text{CuO}_4$  was synthesized by the technique of Refs. 1–3, involving solid-phase reactions among  $\text{La}_2\text{O}_3$ ,  $\text{CuO}$  and  $\text{SrCO}_3$  at  $1000\text{--}1100^\circ\text{C}$  in air. The resulting samples exhibit superconducting properties at  $T \lesssim 36 \text{ K}$ .

The measurements of the second optical harmonic were carried out at room temperature and also when the samples were heated to  $100^\circ\text{C}$  in a constant-temperature cell.

Figure 1a shows the typical shape of the spectrograms of the second optical harmonic that we found. The useful signal is seen to be substantially higher than the noise level. Figure 1, b and c, compares the second-harmonic signals found from the ceramic  $\text{La}_{1.8}\text{Sr}_{0.2}\text{CuO}_4$  and from a plate of a barium titanate single crystal under similar observation conditions. The second-harmonic signal of the barium titanate is 26 times that of the ceramic under study here.

Upon heating, the second-harmonic signal essentially disappears from  $\text{La}_{1.8}\text{Sr}_{0.2}\text{CuO}_4$  at  $\geq 100^\circ\text{C}$ , while in barium titanate a sharp decay of this signal is observed near the ferroelectric phase transition ( $T_c = 130^\circ\text{C}$ ).

Since the matching condition for the second optical harmonic is not satisfied in the barium titanate crystals, the characteristic line corresponding to the region in which the second optical harmonic appears in the reflected light for these crystals is  $l \sim \lambda / 2n \lesssim 0.1 \mu\text{m}$ , where  $n$  is the corresponding refractive index. The depth to which light penetrates into the ceramic sample at the frequency of the second optical har-

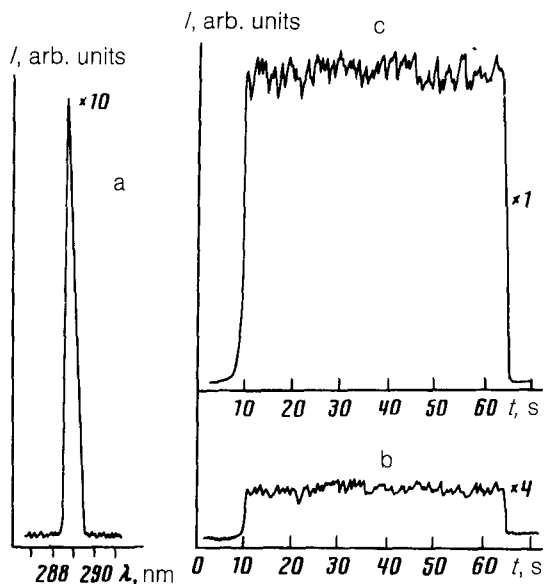


FIG. 1. Signals of the second optical harmonic obtained for the ceramic  $\text{La}_{1.8}\text{Sr}_{0.2}\text{CuO}_4$  and for barium titanate. a—Shape of the spectrogram of the second optical harmonic in  $\text{La}_{1.8}\text{Sr}_{0.2}\text{CuO}_4$ ; b, c—time evolution of the second-harmonic signals in  $\text{La}_{1.8}\text{Sr}_{0.2}\text{CuO}_4$  and  $\text{BaTiO}_3$ , respectively.

monic is on the same order of magnitude:  $l' \sim 1/K$ , where  $K$  is the corresponding absorption coefficient. It can thus be concluded that the optical nonlinearity of the ceramic  $\text{La}_{1.8}\text{Sr}_{0.2}\text{CuO}_4$  is smaller than that in the typical ferroelectric barium titanate by no more than an order of magnitude. At the same time, the optical nonlinearity of materials with an inversion center is usually three or four orders of magnitude smaller than the corresponding value for acentric crystals.

This fact can be explained either in terms of the appearance at  $T \leq 100^\circ\text{C}$  of acentric clusters or by the absence in general of an inversion center in the symmetry group of this ceramic at room temperature. The latter conclusion does not correspond to the data in the literature on the structure of  $\text{La}_{1.8}\text{Sr}_{0.2}\text{CuO}_4$ , according to which the space symmetry group of this material at room temperature is  $D_{4h}^{17}$ . The unit cell in this case corresponds to a nonpolar structure. We might note that the crystal<sup>4</sup>  $\text{La}_2\text{CuO}_4$  is described at temperatures  $T > T_c = 248^\circ\text{C}$  by the same symmetry group ( $D_{4h}^{17}$ ); below this temperature, there is an orthorhombic phase with a symmetry group  $D_{2h}^{18}$  or  $C_{2v}^{18}$ . The latter case corresponds to a polar group. The spontaneous polarization is along the  $c$  axis, i.e., perpendicular to the Cu–O–Cu bonds, along which a metallization occurs. In this connection it might be suggested that regions of a polar phase with a symmetry group  $C_{2v}^{18}$  or regions of some other polar group, which reduces upon the phase transition from a nonpolar group  $D_{4h}^{17}$  as a result of a displacement of ions along the polar ( $c$ ) axis, appear in the ceramic  $\text{La}_{1.8}\text{Sr}_{0.2}\text{CuO}_4$  at  $T \leq 100^\circ\text{C}$ . Judging from the intensity of the observed second-harmonic signal, the relative volume of the polar phase is no more than 5% at room temperature.

In the  $\text{La}_{1.8}\text{Sr}_{0.2}\text{CuO}_4$  samples we also observed a change in the slope of the temperature dependence of the resistance at  $T \sim 140\text{ K}$ . This change may be due to a transition of the bulk of the sample into a polar orthorhombic phase. The appearance

of nucleating regions of this phase at higher temperatures may be caused by a nonuniform distribution of strontium in the sample (in the compound  $\text{La}_2\text{SrO}_4$ , a transition of this sort occurs at  $248^\circ\text{C}$ ). The data thus show the need for refining the symmetry group and phase composition of the ceramic  $\text{La}_{1.8}\text{Sr}_{0.2}\text{CuO}_4$ .

An interesting question here is whether there is a relationship between the high-temperature superconductivity and ferroelectric effects. The fact that several phase states, in particular, a state with a polar order, are realized in the crystals of the family  $(\text{La}_x\text{Sr}_{1-x})_2\text{CuO}_4$  is evidence that the crystal lattices of this family are labile with respect to motions along the  $c$  axis. Correspondingly, in the vibrational spectrum of the crystal we would expect to find low-frequency optical modes or a relaxation continuum of symmetry  $A_1$  below the transition point. If there is a strong interaction of such modes with collective electron excitations which are responsible for the superconductivity, there should be an increase in the temperature of the transition to the superconducting state<sup>7</sup>; this effect might also explain the anomalous increase in  $T_c$  in these materials.

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