

## Enhancement of $T_C$ in 2D $(Ba,K)_2(Pb,Bi)O_4$ with respect to 3D $Ba(Pb,Bi)O_3$

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### Abstract

Superconductivity has been discovered by magnetic susceptibility measurements in the new family of layered oxides  $Ba_{2-x}K_xPb_{1-y}Bi_yO_{4-\delta}$  which do not contain any magnetic ion. In this 2D tetragonal structure,  $T_C$  is found roughly twice higher than in the 3D perovskite with the same bismuth concentration. This is achieved in spite of the fact that the carrier concentration remains lower than in the 3D parent, and that the percentage of bismuth  $y$  does not exceed 15 % in this first series of experiments.

### 1. Introduction

Shortly after the report of the discovery by Bednorz and Müller<sup>1</sup> of high- $T_C$  superconductivity in oxides, the bi-dimensional character of electronic properties was revealed in a single crystal of the parent compound  $La_2NiO_4$  by infrared reflectivity spectroscopy.<sup>2</sup> In the meantime, the isotope effect (shift of  $T_C$  related to atomic mass change) was searched to test the applicability of the BCS theory. But nothing was found for copper, and a very low effect was reported for oxygen (see a review in Ref. 3 for example). Based on these negative results, most groups explored "anything but phonon" theories to explain high- $T_C$  superconductivity. The lack of isotope effect was surprising in view of possible large electron-phonon coupling signature reported in the parent compound  $La_2NiO_4$  investigated by inelastic neutron scattering shortly afterwards.<sup>4,5</sup> A complementary investigation at liquid helium temperature indicated that the branch which corresponds to the breathing mode of oxygen and which shows a strong depression and large broadening at room temperature, is found flat at 4 K.<sup>6</sup> This may be interpreted in terms of signature of electron-phonon coupling because non-stoichiometric  $La_2NiO_4$ , contrary to  $La_2CuO_4$ , is a semiconductor and the electronic concentration is highly temperature-dependent.<sup>7</sup> This is parenthetically the reason why the nickel compound has little chance to become superconductor for lack of mobile carriers able to form Cooper pairs at low temperature. More recent isotope effect measurements<sup>8-11</sup> confirmed the weakness of the effect for the compounds which show highest  $T_C$ 's. But they also showed that the effect is highly dependent upon the electronic concentration. Since  $T_C$  itself is found to depend on the charge carrier concentration too, the conclusion of these latest studies is that electron-

phonon interactions can play a role in the mediation of Cooper pairs, within an Eliashberg model, to explain  $T_C$ 's up to 60-70 K. And a booster has to be found to explain still higher  $T_C$ 's.

### 2. Anharmonic model

Another view of the problem emerges from the scheme of Figure 1 redrawn from Batlogg's plot.<sup>12</sup>

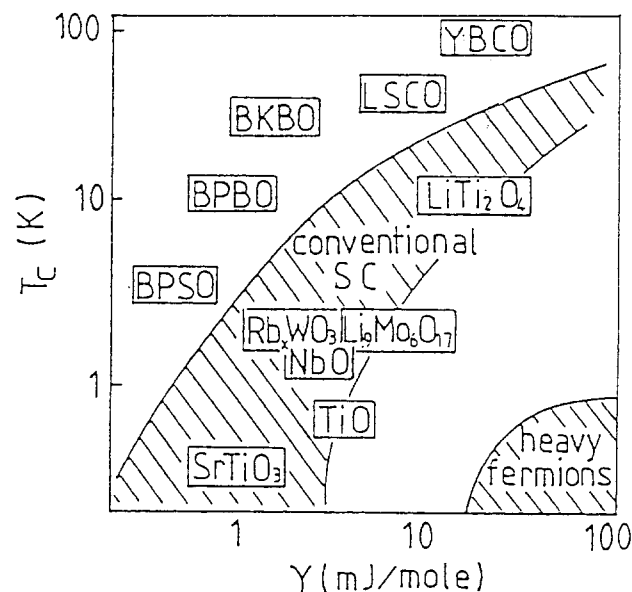


Figure 1 : Schematic trends of critical superconducting temperature versus density of states at Fermi level (adapted from the review Ref. 12). BPSO :  $Ba(Pb,Bi)O_3$ , BPBO :  $Ba(Pb,Bi)O_3$ , BKBO :  $Ba_{0.6}Bi_{0.4}BiO_3$ , LSCO :  $(La,Sr)_2CuO_4$ , YBCO :  $YBa_2Cu_3O_7$ .

Most superconducting oxides are found to lie within the medium range which contains conventional superconductors. Most of them satisfy the Bardeen-Cooper-Schrieffer criteria. It is clear from this plot why the label "high- $T_c$ " is adequate since compounds of the upper part display  $T_c$ 's roughly one order of magnitude larger than the BCS prediction. It has been conjectured that the booster might be highly-anharmonic fluctuations related to (i) the enhanced anisotropic polarisability of oxygen sitting in sandwich between a conducting plane and a reservoir sheet or (ii) the disproportionation of bismuth into more stable  $Bi^{3+}/Bi^{5+}$  pairs with periodic exchange of their mutual charges.<sup>13</sup> Then the lattice would remain polarized during a longer time than when harmonic vibrations are considered as in the basic BCS theory, and be able, therefore, to capture charge carriers more efficiently.

This relaxational-like component of atomic motions is consistent with the weakness of the isotope effect. Finally, the conjecture reproduces the fact that  $T_c$  scales with the electronic concentration, and a crossover from a conventional BCS-Eliashberg regime to a fluctuation-dominated regime was predicted.<sup>13</sup> This model is "universal" in that it allows one to understand why certain oxides lie within the medium conventional range in Figure 1 and why others, with and without magnetic ions, do not. If the conjecture is correct, one expects still higher critical temperatures if both possible origins supposed to enhance  $T_c$  are added. Since one possible origin of anharmonicity is bi-dimensionality, one needs a system of oxides which contain three-dimensional (3D) and bi-dimensional (2D) compounds to test this idea. Copper oxides seems to be excluded since no superconductor has been found in any of the 225 3D copper-based oxides compounds investigated up to now.<sup>14</sup> On the other hand, 3D  $Ba(Pb,Bi)O_3$  and  $(Ba,K)BiO_3$  are known to superconduct up to 13 and 30 K, respectively.  $Ba_2PbO_4$ , on the other hand, is known to exist with the desired  $La_2CuO_4$ -type tetragonal structure. Unfortunately,  $Ba_2PbO_4$  is an insulator.<sup>15</sup> We tried, therefore, to substitute potassium onto the baryum site to inject charge carriers.

### 3. Synthesis and characterization of new materials

The solid solution  $Ba_2Pb_{1-y}Bi_yO_4$  gives a single phase with the tetragonal structure up to  $x = 0.3$ . The materials remain insulating for any  $y$ . The tentative formula  $Ba_2BiO_4$  has been found, on the other hand, to crystallize actually in a 3D double perovskite structure of formula  $Ba_2(Ba_{2/3}Bi^{III}_{1/3})Bi^VO_{6-\delta}$  and the compound - is an insulator.<sup>16</sup> Several attempts to

synthesize  $Ba_{2-x}K_xPb_{1-y}Bi_yO_4$ , by conventional solid state reaction were unsuccessful. Only a modified sol-gel route<sup>17</sup> allowed us to obtain the conducting materials. Subsequent annealing under oxygen at 450°C was necessary to ensure best conductivities. Only powders showing a single phase in X-ray diagrams were studied further. The substitution allows the atomic sheet to play the role of charge reservoir, and ensures a concentration of mobile charges of the order of  $1-4 \cdot 10^{20} \text{ cm}^{-3}$ . The carrier concentrations are estimated from the screening of phonons by the plasmon deduced from the analysis of infrared reflection spectra.<sup>18</sup>

### 4. Superconductivity

Figure 2 shows the magnetic susceptibility of several compounds of the family. The marked decrease below zero cannot be assigned to a phenomenon other than superconductivity since no magnetic ion is present in any of the compounds.

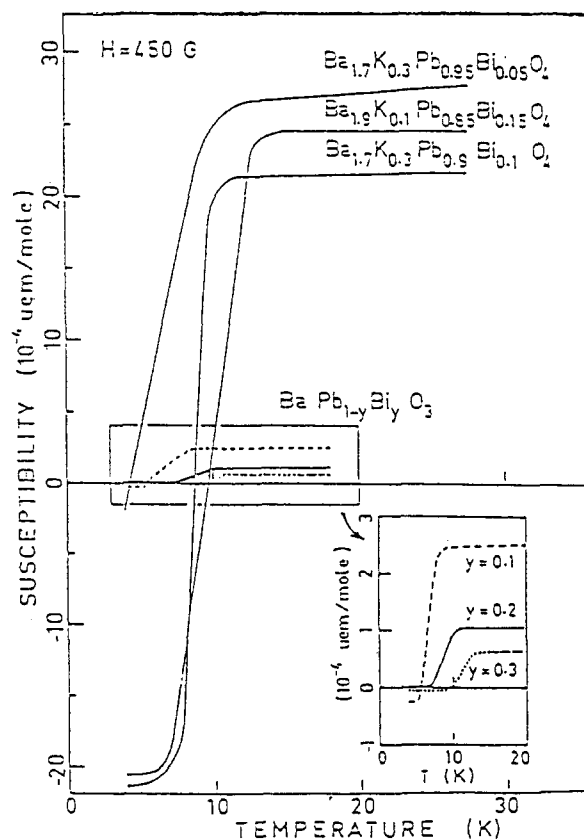


Figure 2 : The temperature dependence of the magnetic susceptibility of the tetragonal conducting compounds compared to that of perovskites measured in the same conditions.

Note that the amplitude of the signal is reduced by the magnetic field of 450 G, under which the experiments have been performed, because it is probably larger than  $H_{C1}$ . We have synthesized and re-measured in the same conditions 3D compounds Ba(Pb,Bi)O<sub>3</sub> for comparison. Results are consistent with published data. Note that the amplitude of the positive part of the signal in 3D phases is some 12-15 times smaller than in our 2D systems. This low level is probably due to the electronic concentration in Ba(Pb,Bi)O<sub>3</sub> which is one order of magnitude larger than in 2D compounds. The results are therefore not due to 3D impurity phases.

$T_c$  is found to increase with the bismuth concentration.  $T_c$  (onset) = 9, 12.5 and 14 K for  $y = 0.05$ , 0.1 and 0.15, respectively, in Ba<sub>2-x</sub>K<sub>x</sub>Pb<sub>1-y</sub>Bi<sub>y</sub>O<sub>4-δ</sub>. The highest  $T_c$  has been obtained with  $x = 0.1$ . More interesting is to realize that, for a given bismuth rate, for example  $y = 0.1$ ,  $T_c$  is found twice higher in the 2D compound compared to the 3D structure.

### 5. Lattice vibrations

The imaginary part of the dielectric response deduced from infrared reflectivity measured in the infrared, is shown in Figure 3 and compared with the insulator parent without potassium.

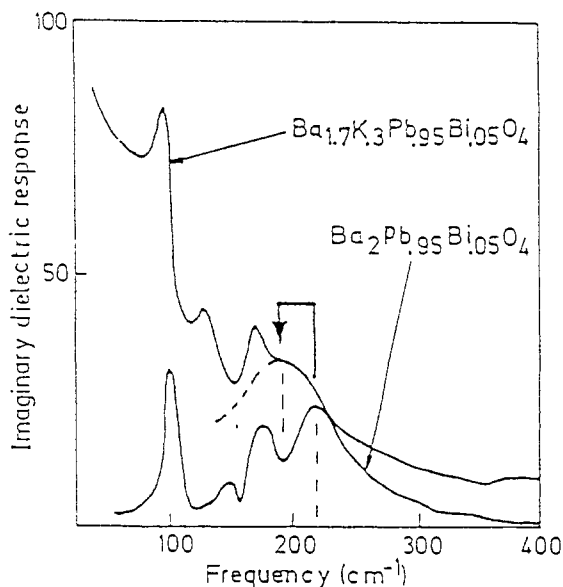


Figure 3 - Incipient softening of the  $A_{2u}$  TO mode with the onset of charge carrier concentration (visualized by the plasma background).

$E_u$ -type vibrational modes polarized within the conducting (a,b) plane are partially screened by the charge carrier background. The  $A_{2u}$ -type modes are unscreened as shown by best data fit.<sup>18</sup> It is instructive to consider the downshift and broadening of the main  $A_{2u}$  mode denoted by an arrow in Figure 3.

We interpret it as the signature of onset of instability related to the possible (dynamic) double-well potential which would appear when the apical oxygen is submitted to a local electric field, the intensity of which is related to the charge carrier concentration, according to our conjecture summarized above,<sup>13</sup> and consistent with double-well potential seen at apical oxygen site deduced from EXAFS measurements.<sup>19</sup>

### 6. Conclusion

The discovery of the first family of layered oxide superconductors without any magnetic ion is worth mentioning. Superconductivity is obtained at a temperature which is roughly twice larger than in the cubic perovskite with same bismuth rate. This is achieved in spite of the fact that the carrier concentration estimated from both Drude reflectivity and magnetic susceptibility level in the normal phase, is significantly lower than in the perovskite analogues. The bi-dimensionality of the structure is thus confirmed to be a favourable ingredient and results support our anharmonic model which focus in particular on the specific role possibly played by the apical oxygen and dynamic bismuth disproportionation.

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