Effect of molecular dimerization and tetramerization on charge ordering pattern in highly-correlated organic compounds.

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Various charge ordering(CO) pattern including $2k_F$ and $4k_F$ have been proposed for $(TMTTF)_2X$. The crystal structure of quasi one-dimensional compounds $(TMTTF)_2X$ is triclinic(P-1) and TMTTF molecules on general positions forms a molecular dimer, but the counter anion X is located on *inversion center* of the unit cell. When the anion X is not centro-symmetric thereby the X has orientational degree of freedom in the crystal. While disordered at room temperature, the X will be ordered to gain entropy term by cooling. Solving many low temperature structures and superstructures, we noticed some relation between the magnitude of the molecular dimerization and CO pattern in $(TMTTF)_2X$. Here we presents the relation between CO and molecular dimerization and tetramerization, which has been verified by recent experiment for $(TMTTF)_2X(X=ClO_4$ and $FSO_3)$.

For this small volume of the sample, we often used low temperature vacuum camera(LTVAC) in BL02B1. The conditions of structure and superstructure analyses were usually very good: typical R-factors are between 2.0% and 4.5%. To evaluate the charge modulation amplitude(ρ), we calculated the ionicity of each TMTTF molecule using bond lengths and TMTTF HOMO levels using atomic positions obtained by X-ray superstructure.

By cooling the magnitude of molecular dimerization in transfer integral between HOMO tends to decrease. When the dimerization becomes less than 0.25, the $4k_F$ CO observed in $(TMTTF)_2X(X=PF_6$, AsF_6, SbF_6 and SCN). On the other hands, the insulating state around RT in above compounds will be dimer Mott phase like kappa-ET compounds. This competition between $4k_F$ CO and dimmer Mott phase will be consistent with the theory. As a result of anion ordering, prominent molecular tetramerization reaching 0.2-0.3 has been observed together with $2k_F$ CO in $(TMTTF)_2X(X=ReO_4$ and $FSO_3)$. But no tetramerization and no $2k_F$ CO in X= ClO_4. In short, strong dimerization hinders $4k_F$ CO and strong tetramerization grows $2k_F$ CO. We can clearly visualize the CO phase diagram as a function of dimerization and tetramerization in the Figure.

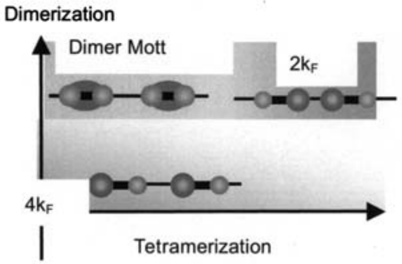

Figure Schematic phase diagram of the electronic states including CO for $(TMTTF)_2X$.

Relationship between 2212 intergrowths density, Pb substitution for Ca site and sintering condition in the $(Bi,Pb)_2Sr_2Ca_2Cu_3O_{10+\delta}$ phase

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High T_c superconducting cuprate, $(Bi,Pb)_2Sr_2Ca_2Cu_3O_{10-\delta}$((Bi,Pb)2223) have been researched and developed for practical application of high performance superconducting cables. However, in spite of its outstanding potential, performance of recent (Bi,Pb)2223 cables is limited by several factors. (Bi,Pb)2223 has intergrowths of the 2212 subcell with one less Cu-O and Ca layer than the (Bi,Pb)2223 subcell. The 2212 phase has lower Tc so that the critical current density in a (Bi,Pb)2223 grain is suppressed if high density of 2212 intergrowths is contained.

We have reported about the origin of 2212 intergrowths with in-situ synchrotron XRD measurement [1]. We investigated 2212 intergrowths density by considering change of anisotropic strain to ci-axis in the (Bi,Pb)2223 phase. However, it is still unclear how sintering conditions influence 2212 intergrowths formation. In this study, we investigate the relationship between 2212 intergrowths density and sintering condition.

The XRD measurements were carried out with the beam energy 53 keV. θ-2θ scan was performed and the data was analyzed by the Rietveld method with RIETAN 2000 software [2].

Fig.1 demonstrates one of results showing the Relationship beween 2212 intergrowths and Pb substitution via sintering temperature. As seen in Fig.1, the density of 2212 intergrowths decreased as sintering temperature became higher, whereas Pb substitution for Ca site increased. As indicated in Ref.[1], 2212 intergrowths tend to be contained to high density when the liquid phase formation is not uniformed and its chemical composition fluctuates. In addition, Pb substitution leads to form homogeneous (Bi,Pb)2223 phase. Therefore Fig.1 shows that Pb cation help the liquid phase uniformed, and Pb substitution makes the (Bi,Pb)2223 phase less 2212 intergrowths. Further investigation and detailed analysis of data are now proceeding.

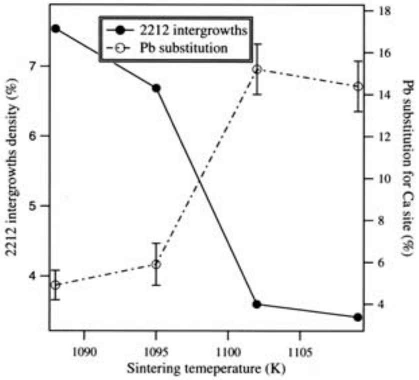

Fig.1 Relationship between 2212 intergrowth density and Pb substitution for Ca site

[1] Nakao F and Osamura K 2005 *Supercond. Sci. Technol.* **18** 513-520

[2] Izumi F and Ikeda T 2000 *Mater. Sci. Forum* **321-324** 198-205