Phase Stability and Electronic Properties of $Bi_2BaLnCuO_{6+\delta}$ Cuprates with Structure 2201 Type

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The synthesis of new bismuth-barium containing members of layered cuprates with 2201 type structure was reported. By solution calorimetry the formation enthalpies for $Bi_2MLaCuO_{6.5}$ ($M = Ba$, $Ba_{0.5}Sr_{0.5}$, Sr) were obtained. Crucial influence of partial oxygen pressure and size of lanthanoid on stability of layered cuprates was shown. Electronic states of variable valence atoms were studied by voltammetry of solids.

Introduction

The investigations of substitution chemistry and stability range of layered bismuth cuprates with 2201 ($Bi_2Sr_2CuO_6$) and 2212 (Bi_2 Sr_2 $CaCu_2O_8$) type structures have been performed very intensively.[1~9] A large number of new phases were obtained by full or partial substitution of metals in all crystallographic sites: of Bi by Pb, Tl, of Sr by Ln, Ca, Bi, of Cu by Fe, Co, Mn, Ni. But despite intensive research layered bismuth cuprates containing barium atoms were obtained recently.[10~13] The properties of barium containing phases differ remarkably from strontium ones. First of all barium phases are less stable comparing with their strontium analogs when cationic composition and partial oxygen pressure is changed. Layered cuprates formed in Bi-Ba-Ln-Cu-O systems can be considered as a model to understand stability problem of complex phases. These phases are attractive also by reason of absence of superconducting properties, while their strontium analogs are superconducting.

In this paper we report the results of synthesis, study of solubility ranges, stability, and electronic properties of barium phases with 2201 type structure. We compare also their properties with those for isostructural strontium phases.

Experimental

Synthesis and characterization of samples. All samples were prepared from high purity powders of Bi_2O_3, $BaCO_3$, $SrCO_3$, PbO, Ln_2O_3 ($Ln = La$, Pr, Nd, Sm, Eu, Gd, and Y), CeO_2 and CuO by conventional solid state procedure in Ar atmosphere. Residual oxygen pressure in argon was less than 10^{-4} atm. Experimental details are described elsewhere.[13] Oxygen content was determined by iodometric titration.[14] The resistivity was measured by conventional 4th-probe method.

Calorimetric measurements. Samples $Bi_2BaLaCuO_{6.49(2)}$, $Bi_2Ba_{0.5}Sr_{0.5}LaCuO_{6.50(2)}$, $Bi_2SrLaCuO_{6.50(2)}$ Bi_2O_3, $BaCO_3$, $SrCO_3$, La_2O_3 and CuO were used for calorimetric measurements. The solution calorimetry method was used. The solutions of 6 M HCl were used as solvents in all the runs. All experiments were performed at 323 K. Details of calorimetric experiments were described elsewhere.[15]

Voltammetry experiments. The voltammetric study

technique was described by Zakharchuk *et al*[16] and at this point it has been used without modifications. Hydrochloric acid solution was used as background electrolyte. Voltammetric curves were registered by universal polarograph OH-105 (Hungary). The rate of potential scanning was equal to 16.7 mV/s. Cu_2O, CuO, PbO, Bi_2O_3, $KBiO_3$, $BaBiO_3$, Ca_2PbO_4, and $BaPbO_3$ were used as test compounds for the identification of various valence states of Cu, Bi, Pb, O atoms in the phases with 2201 structure.

Results

Synthesis of $Bi_2BaLnCuO_{6+\delta}$($Ln = La$, Pr, Nd) samples and $Bi_2Ba_{2-x}LaxCuO_{6+\delta}$ solid solution. We have studied $Bi_2BaLnCuO_{6+\delta}$ series ($Ln = La$, Ce, Pr, Nd, Sm, Eu and Gd). Syntheses in air or oxygen for all samples in Bi-Ba-Ln-Cu-O systems give dark-brown or grey mixtures. XRD patterns show the presence of perovskite-like phase and CuO as the main components. Annealing in argon atmosphere results in the formation of phase for lanthanum, praseodymium and neodimium with cell parameters $a = 5.494$ Å, $b = 5.524$ Å, $c = 24.21$ Å for La $a = 5.514(5)$ Å, $c = 23.95(4)$ Å for Pr, and $a = 5.487(5)$ Å, $c = 24.18(4)$ Å for Nd. For $Ln = Sm$, Eu, Gd and Y the complex mixture containing $BaBiO_3$-like phase, CuO and some unidentified phases was found as the main products. Cerium sample has unusually low melting point (below 600 ℃) in inert atmosphere, $BaCeO_3$ and CuO are main products, no trace of 2201 phase was found. Magnetic and resistive measurements of $Bi_2BaLnCuO_{6+\delta}$ ($Ln = La$, Pr, Nd) samples demonstrated that they all do not show superconductivity down to 4 K.

We have investigated $Bi_2Ba_{2-x}La_xCuO_{6+\delta}$ section. The dependence of the cell parameters of 2201 type phase for the samples $Bi_2Ba_{2-x}La_xCuO_{6+\delta}$ *vs.* composition is shown in Figure 1. These data along with X-ray diffraction analysis make a sound basis to conclude that the range of solubility for Bi_2Ba_{2-x} $La_xCuO_{6-\delta}$ solid solution is $0.8 \leq x \leq 1.2$. It is remarkably narrower than that for the $Bi_2Sr_{2-x}La_xCuO_{6+\delta}$ ($0.1 < x < 1.3$) solid solution.[4] The restriction of the range of solubility of $Bi_2Ba_{2-x}La_xCuO_{6+\delta}$ at the barium-rich side, as compared with $Bi_2Sr_{2-x}La_xCuO_{6+\delta}$, can be explained by the inversion of relative stability of the phases with the structures of 2201 and $BaBiO_3$ types. When barium content in sample exceeds
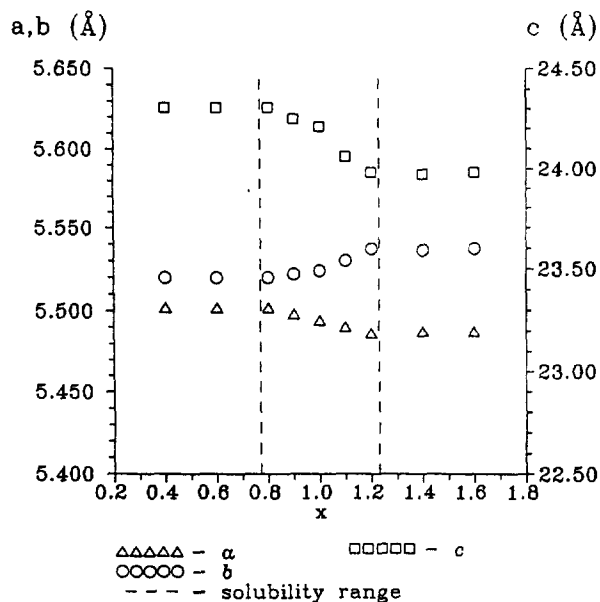
**Figure 1.** The cell parameters *vs.* composition in $Bi_2Ba_{2-x}La_x$ $CuO_{6+\delta}$ samples.

Table 1. Enthalpies of formation of phases $Bi_2MLaCuO_{6.5}$ from oxides and elements and their lattice energy

Phase	$\Delta H^0_{323}(2)$, kJ	$\Delta H^0_{f,323}$, kJ	E, kJ
$Bi_2BaLaCuO_{6.5}$	-17 ± 5	-2201	26565
$Bi_2Ba_{0.5}Sr_{0.5}LaCuO_{6.5}$	-11 ± 5	-2217	26645
$Bi_2SrLaCuO_{6.5}$	0 ± 5	-2227	26717

1.2 the 2201 phase decomposes to yield perovskite-like Ba-BiO phase. As for lanthanum rich side, it does not differ much from that in $Bi_2Sr_{2-x}La_xCuO_{6+\delta}$. The variation of the Ba/La ratio affects the cell dimensions in such way that the orthorhombic b-a distortion increases with increasing lanthanum content, half-sum $(a+b)/2$ remaining unchanged and c parameter steadily decreasing within the range of solubility.

Refinement of structure of phase $Bi_2BaLaCuO_{6.5}$ based on integrated intensities supports model of 2201 type structure. Essential feature of the structure is unusually large Cu-O distance in CuO_2 plane, namely, 1.946(1) Å. This distance is the largest known for this structure type (compare e.g. with that in $Tl_2Ba_2CuO_{6\pm\delta}$: 1.934(1) Å[17]).

Formation enthalpy of phases with 2201 type structure. The measured enthalpies of dissolution were used for the enthalpy calculation for reaction (1).

$$Bi_2O_3 + CO_3 + 1/2\ La_2O_3 + CuO = Bi_2MLaCuO_{6.5} + CO_2 \quad (1)$$
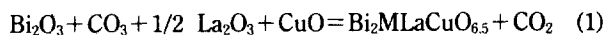
where M is Ba, $Ba_{0.5}Sr_{0.5}$, and Sr.

Literature data[18] for the heats of reaction $MO + CO_2 > MCO_3$ and for standard enthalpies of formation of Bi_2O_3, $BaCO_3$, $SrCO_3$, La_2O_3 and CuO were used to calculate the enthalpy of formation of $Bi_2MLaCuO_{6.5}$ from individual oxides (2) and from elements.

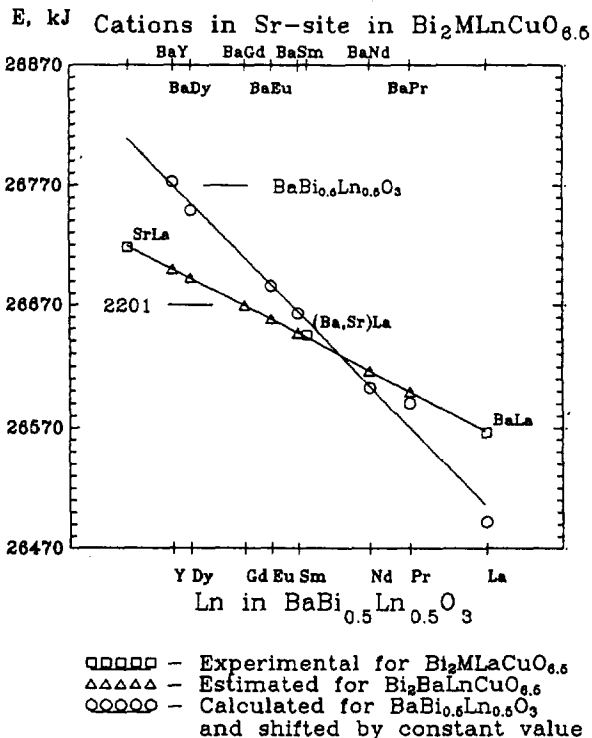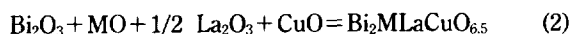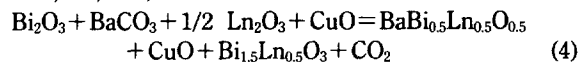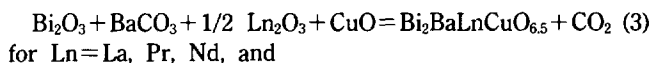$$Bi_2O_3 + MO + 1/2\ La_2O_3 + CuO = Bi_2MLaCuO_{6.5} \quad (2)$$

Figure 2. Lattice energies of phases with 2201 and ABO_3 type structures *vs.* average radii of cations in Sr and B-sites.

The values of enthalpy of formation of $Bi_2MLaCuO_{6.5}$ phases from oxides together with calculated standard enthalpies of formation for these phases are presented in Table 1. It is noteworthy that values of formation enthalpies of these phases are very close.

Thermodynamic modeling for reaction Bi_2BaLn-$CuO_{6.5} = BaBi_{0.5}Ln_{0.5}O_{2.5} + CuO + Bi_{1.5}Ln_{0.5}O_3$. The interaction of starting compounds for different rare earth elements goes in two different ways depending upon the nature of starting materials.

$$Bi_2O_3 + BaCO_3 + 1/2\ Ln_2O_3 + CuO = Bi_2BaLnCuO_{6.5} + CO_2 \quad (3)$$

for Ln=La, Pr, Nd, and

$$Bi_2O_3 + BaCO_3 + 1/2\ Ln_2O_3 + CuO = BaBi_{0.5}Ln_{0.5}O_{0.5}$$
$$+ CuO + Bi_{1.5}Ln_{0.5}O_3 + CO_2 \quad (4)$$

for Ln=Sm, Eu, Gd, Y.

It is difficult to explain these experimental observations experimental facts by crystal-chemical restrictions imposed by the nature of 2201 type structure phase only. The 2201 type structure phase can be realized for various combinations of cations in the Sr-site: $BaLa^{12,13}$ (R_{av}=1.483 Å), $SrLa^4$ (R= 1.403 Å), and $CaLa^9$ (R_{av}=1.338 Å). Thus, $Bi_2BaSmCuO_{6+\delta}$ phase (R_{av}=1.441 Å), being within this interval of average radius, should be stable.

Evidently, the possibility to form the 2201 type structure for various lanthanoids is determined by the sign of Δ_r G for reaction (5):

$$Bi_2BaLnCuO_{6.5} = BaBi_{0.5}Ln_{0.5}O_{2.5} + CuO + Bi_{1.5}Ln_{0.5}O_3 \quad (5)$$
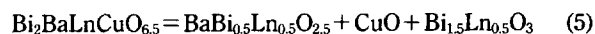
The direction of chemical reaction is defined by the sign of standard change in Gibbs free energy. The absence of
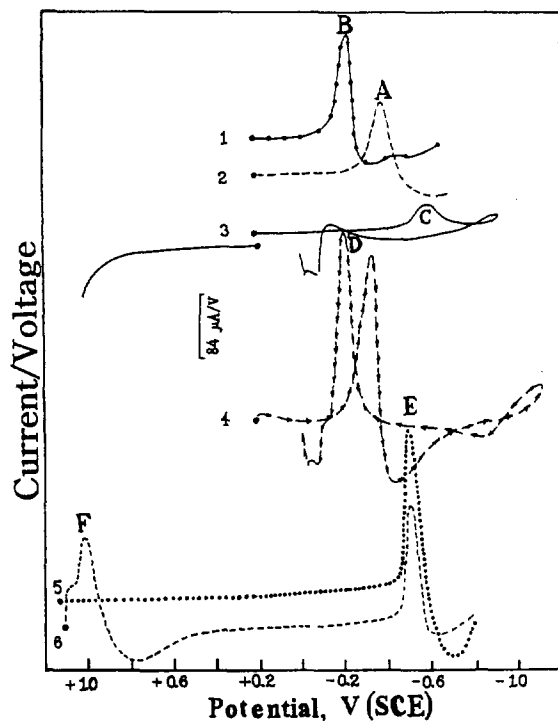
Figure 3. Differential cathodic curves of the electrochemical conversions of $Cu_2O(1)$, $CuO(2)$, $Bi_2O_3(3)$, $KBiO_3(4)$, $PbO(5)$ and $BaPbO_3(6)$ on the graphite paste electrode. $C_{sample} - 1 \cdot 10^{-5}$ mol/g of the paste $C_{background\ electrolyte} - 0.05$ M HCl.

experimental data for thermodynamic properties of all Bi_2Ba-$LnCuO_{6.5}$, $Bi_{1.5}Ln_{0.5}O_3$, and $BaBi_{0.5}Ln_{0.5}O_{2.5}$ phases (most of them were not obtained) made us to build our considerations on the basis of lattice energies using some assumptions discussed in.[15] The lattice energy of a phase can be calculated as:

$$E_T = -\Delta H^0_{f,T} + \Sigma v_i \Delta H^0_{f,T}(M_i,^{q+})_g + v_0 H^0_{f,T}(O_g^{-2}) \quad (6)$$

where $\Delta H^0_{f,298}$ standard formation enthalpy of the phase,
v_i stoichiometric coefficient at metal i,
v_0 stoichiometric coefficient at oxygen,

$\Delta H^0_{f,298}(M_i,^{q+})$ standard formation enthalpy of metal ion, and $\Delta H^0_{f,298}(O^{2-})_g$ standard formation enthalpy of O^{2-} ion.

The lattice energies of $Bi_2MLaCuO_{6.5}$ (M=Ba, $Ba_{0.5}Sr_{0.5}$ and Sr) phases can be calculated from experimental values of formation enthalpies using equation (6) and the data.[19] The results are presented in Table 1. The lattice energies of Bi_2 $BaLnCuO_{6.5}$ phases can be estimated from dependencies of lattice energies on average ionic radii in the Sr site. The values of lattice energies of perovskite-like phases were calculated by Born-Meier equation using Madelung constant[20] and cell parameters taken from literature.[21]

Figure 2 presents the dependencies of lattice energy for 2201 and $BaBi_{0.5}Ln_{0.5}O_3$ type phases on the nature of rare earth metals in the Sr and Bi site, respectively. From Figure 2 it can be seen that the lattice energy of the perovskite phase decreases more steeply than that of 2201 phase. This difference seems to govern the relative stability of ABO_3 and 2201 phases when rare earth element is changed.
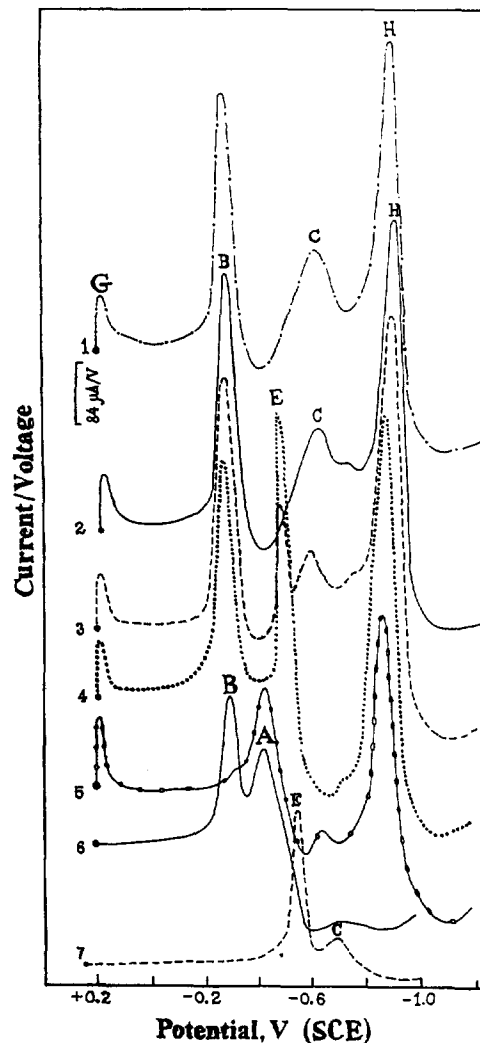

Figure 4. Differential cathodic curves of the electrochemical conversions of $Bi_2SrLaCuO_{6.50}(1)$, $Bi_2BaLaCuO_{6.49}(2)$, $Bi_{1.5}Pb_{0.5}$ $BaLaCuO_{6.24}(3)$, $BiPbBaLaCuO_{6.00}(4)$, $Bi_2Sr_{1.6}La_{0.4}CuO_{6.33}(5)$, $\{Cu_2O + CuO\}(6)$, and $\{PbO + Bi_2O_3\}(7)$, on the graphite paste electrode. $C_{sample} - 1 \cdot 10^{-5}$ mol/g of the paste, $C_{background\ electrolyte} - 0.05$ M HCl.

Voltammetric study of phases. The oxidation states of the alkaline earth and rare earth metals were assumed as 2+ and 3+, respectively, as their usual oxidation states. The oxidation states of the varying valence elements have been ascribed on basis of the set of experimental electrochemical data for the reference substances. Details of voltammetric study will be described elsewhere[22] and experimental curves for testing compounds are shown in Figure 3.

Electronic states of copper atoms in CuO and Cu_2O were accepted as Cu^{2+} and Cu^+ (signals A and B), states of bismuth atoms in Bi_2O_3 and $KBiO_3$ phases-as Bi^{3+} and Bi^{5+} (signals C and D), states of lead atoms in PbO and $BaPbO_3$ (Ca_2PbO_4 also)-as Pb^{2+} and Pb^{4+} (signals E and F).

It should be pointed out that there are notable difficulties for identification of unusual O^--type electronic states (peroxytonic) owing to the solid reference samples are absent. Consequently the oxidation state of oxygen was interpreted by a type of the electrode reactions on the +(1.0 0.1) V range

Electronic Properties of Barium Phases with 2201 Type Structure

Bull. Korean Chem. Soc. **1995**, Vol. 16, No. 6   487

(signal G in Figure 4).[22]

In Figure 4 the differential cathodic curves for phases with 2201 structure with different cationic composition along with those for ($CuO + Cu_2O$), ($PbO + Bi_2O_3$) mixtures are presented. Analysis of experimental curves allows to ascribe electronic state of copper for phase $Bi_2BaLaCuO_{6+}$ as Cu. Substitution of barium by strontium does not change electronic states of atoms. But comparison of cathodic curves of Bi_2Ba-$LaCuO_{6.49}$ ($Bi_2SrLaCuO_{6.50}$) with that of $Bi_2Sr_{1.6}La_{0.4}CuO_{6.33}$ reveals essential difference of electronic states of copper atoms in these phases. As in $Bi_2BaLaCuO_{6.49}$ and $Bi_2SrLaCuO_{6.50}$ phases the electronic state of copper atoms can be ascribed as Cu^+ (signal B), in $Bi_2Sr_{1.6}La_{0.4}CuO_{6.33}$ the electronic state of copper atoms is close to Cu^{2+} (signal A).

Broad signal C with low intensity in $Bi_2BaLaCuO_{6.5}$ is typical for Bi^{3+} states. Similar signal appeared during reduction of Bi_2O_3 (curve 3 in Figure 3). In the curve of electrochemical reduction of $Bi_2BaLaCuO_{6.5}$ there is another signal attributed to Bi states (signal H). Earlier this state was described as Bi^{2+} state.[22]

While this phase contains two unequivalent bismuth atoms, we have studied by voltammetry of solids the solid solution $Bi_{2-x}Pb_xBaLaCuO_{6+\delta}$ described earlier.[13]

On cathodic curves of samples $Bi_{2-x}Pb_xBaLaCuO_{6+\delta}$ ($x>0$) (Figure 4, curves 3, 4) the signal E attributed to reduction of Pb^{2+} state is appeared. Investigation of voltammetric curves at $1.2+0$ V clearly show absence any Pb^{4+} states in single phase samples. From comparison of these curves one can see that the intensity of peak attributed to Pb^{2+} states is increased. However the intensity of peak attributed to Bi^{3+} is decreased becoming to zero at composition $BiPbBa$-$LaCuO_{6.0}$ which is limit of this solid solution. Oxygen content is monotonically decreased in agreement with substitution $Bi^{3+} \rightarrow Pb^{2+}$. There are not any changes of the position and amplitude of the signals attributed to another Bi-state, copper, and O^- state reduction within experimental accuracy.

Discussion

Stability of phases. Comparison of phase composition for a large set of syntheses in Bi-Ba-Ln-Cu-O systems both in and out the 2201 section shows that the main impurity phase in these systems is perovskite-like phase having variable composition. Probably, change of Gibbs free energy of this perovskite-like phase, rather than of other phases in these systems, defines the possibility of formation of 2201 phases under different experimental conditions.

Dependence on partial oxygen pressure. Layered cuprates with 2201 type structure in Bi-Ba-Ln-Cu-O systems demonstrate a strong dependence of the stability on partial oxygen pressure and cannot be prepared at $P_{O2}=0.21$ atm. To a certain degree, this dependence is less inherent for layered cuprates formed in Bi-Sr-Ln-Cu-O systems, where 2201 type phases are stable in a wide range of oxygen pressure. The observed difference in the stability between barium and strontium phases with 2201 structure is due to the distinction between Ba-Bi-O and Sr-Bi-O phase diagrams. In the Sr-Bi-O phase diagram (at $P_{O2}=0.21$ atm and lower) no stable perovskite-like phase occurs, and the single $Sr_2Bi_2O_5$[23] phase having Bi^{3+} state is the only phase formed near $SrBiO_x$

composition. In the Ba-Bi-O phase diagram the $BaBiO_3$[24] phase occurs which is stable in a wide range of partial oxygen pressure. In a similar manner while $Sr_2Bi^{5+}Ln^{3+}O_6$ phases are formed in Sr-Bi-La-O systems at elevated oxygen pressure more than 2 atm., their Ba analogs are stable in inert atmosphere. These distinctions result in extension of the solubility range for $Bi_2Sr_{1.6-x}Ba_xLa_{0.4}CuO_{6+\delta}$ solid solution (from $x=0.4$ up to at least $x=0.8$) caused by decrease in oxygen pressure (from 0.21 atm down to 10^{-4} atm[25]).

Therefore, the decrease of oxygen partial pressure destabilizes perovskite-like phase due to the reduction of Bi^{5+} to Bi^{3+}, while increasing the phase stability of the 2201 and 2212 type structure.

Influence of the portion of trivalent cation in Sr-site. Partial substitution of the strontium by lanthanum stabilizes 2201 phase in Bi-Sr-La-Cu-O system. For instance, stoichiometric $Bi_2Sr_2CuO_{6+\delta}$ with "ideal" 2201 type structure cannot be synthesized at free oxygen atmosphere, but a little substitution of strontium by lanthanum leads to the formation of "ideal" 2201 phase.[4]

In Bi-Ba-La-Cu-O system 2201 structure type phase is stable at high concentration of lanthanum only. When portion of La is less than 0.8 $Bi_2Ba_{2-x}LaxCuO_{6+\delta}$, solid solution decomposes forming perovskite-like phase. This fact can be explained considering the change of lattice energies of 2201 and ABO_3 phases. Substitution of Ba^{2+} by La^{3+} in 2201 increases lattice energy of 2201 phase due to Madelung term. But in $Ba_2Bi^{5+}(Bi^{3+})_{1-x}(La^{3+})_xO_6$ phase La ions occupy Bi^{3+} site and lattice energy of this phase remains virtually unchanged.

Influence cation's radii. 2201 type structure phases in Bi-Ba-Ln-Cu-O systems were obtained for large rare earth metals only. In other investigated systems the perovskite-like phases are formed. The reason of that consists in different dependencies of lattice energy of phases upon nature of Ln (Figure 2). Lattice energy of complex multilayered 2201 phase changes only slightly with change cation's radius. Packing efficiency of perovskite-like phase $BaBi_{0.5}Ln_{0.5}O_3$ increases substantially with the decrease in lanthanoid radius in a series of $BaBi_{0.5}La_{0.5}O_3$, $BaBi_{0.5}Pr_{0.5}O_3$, ⋯, $BaBi_{0.5}Y_{0.5}O_3$. This leads to stabilization of perovskite-like phases for Ln = Sm, Eu, ⋯, Y in Bi-Ba-Ln-Cu-O systems. There is no traces of 2201 phase in Ce sample, despite ionic radius of Ce^{3+} is between those of La and Pr. But through relatively low forth ionization potential of cerium $BaCe^{4+}O^3$ is realized under given experimental conditions instead of $Bi_2BaCe^{3-}CuO_{6+\delta}$ or $BaBi_{0.5}^{5+}Ce_{0.5}^{3+}O_3$.

It should be noted that the substitution of barium by strontium and of lanthanum by other lanthanoids affects stability of 2201 phase in different way. In 2201 phase both rare earth and alkaline earth cations fill common crystallographic site (Sr-site).[7] And substitution of barium by strontium and lanthanum by lanthanoids must increase the lattice energies of this phases in a similar manner (equal average ionic radius results in equal lattice energy). In perovskite phase $BaBi_{0.5}La_{0.5}O_3$ barium and lanthanoids fill different crystallographic sites: Ba fills A site (CN = 12 for ideal perovskite) and lanthanoid fills part of B-site (CN = 6 for ideal perovskite).[26] Evidently, the substitution of barium and of lanthanum will differently affect the lattice energy. This different
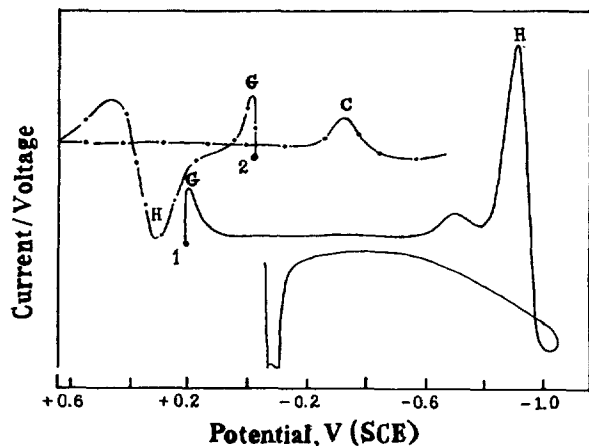
Figure 5. Differential cathodic-anodic (1) and anodic-cathodic (2) curves of the electrochemical conversions of $BaBiO_3$ on the graphite paste electrode. $C_{sample} - 1 \cdot 10^{-4}$ mol/g of the paste, $C_{background\ electrolyte} - 0.05$ M HCl.

behavior of stability of perovskite-like phase on the substitution of barium and lanthanum is correlated with tolerance factor.[13]

Electronic states of atoms. Data of electrochemical study show essential distinction in the electronic states of copper atoms in $Bi_2BaLaCuO_{6.5}$ ($Bi_2SrLaCuO_{6.5}$) and $Bi_2Sr_1La_{0.4}$ $CuO_{6+\delta}$ phases. This distinction correlates qualitatively with change in Cu-O distances in CuO_2 layer or with change cell parameters of these phases in ab plane. The substitution of alkaline earth metal M^{2+} by rare earth metal Ln^{3+} results in decrease of charge of copper atoms. Excess of electronic density occupies antibonding orbital of Cu-O bond resulting in Cu-O distance increase in CuO_2-layer, and, consequently, to increase of a and b parameters. We suppose that distinction in electronic states of copper in $Bi_2BaLaCuO_{6.5}$ (Bi_2SrLa-$CuO_{6.5}$) and $Bi_2Sr_{1.6}La_{0.4}CuO_{6+\delta}$determines distinction in superconducting properties. Charge transfer from oxygen to variable valence metals is common for oxide HTSC,[27] and the model of a local electron transfer is preferable for such phases.[28,29]

State related to signal H is unusual. This state cannot be described neither as Bi^{3+} nor as Bi^{5+}. Bismuth atoms having this state undergo both reduction and oxidation in electrochemical experiments (Figure 5) forming Bi^0 and Bi^{3+}, respectively.[22] We describe this state as Bi^{2+}.

So, all experimental data reveal that the insight of phase $Bi_2BaLaCuO_{6.49}$ using "usual" valence states as $(Bi^{3+})_2Ba^{2+}La^{3+}$ $Cu^{2+}(O^{2-})_{6.5}$ satisfies charge balance, but is not adequate and doesn't explain the experimental data. Taking into account that

1) copper presents as Cu^+,

2) there are two different states of Bi atoms: one is close to Bi^{3+}, another can be described as Bi^{2+}.

3) intensity of Bi^{3+} signal becomes to zero at composition $BiPbBaLaCuO_{6+\delta}$, so ratio Bi^{3+}/Bi^{2+} is supposedly equal to 1,

4) "peroxytonic" states O^- are present in phase, Bi_2BaLa-$CuO_{6.49}$ phase can be described by formula $Bi^{3+}Bi^{2+}Ba^{2+}La^{3+}$ $Cu^+(O^{2-})_{4.5}(O^-)_2$. This formula reflects the features of elec-

trochemical behavior phase in voltammetric experiments. In similar manner, the solid solution $Bi_{2-x}Pb_xBaLaCuO_{6+\delta}$ can be described by formula $Bi^{3+}_{1-x}Pb^{2+}_xBi^{2+}Ba^{2+}La^{3+}Cu^+(O^{2-})_{4.5-0.5x}$ $(O^-)_2$.

In summary, relative stability of 2201 structure type phase and perovskite-like phase defines possibility of formation of layered cuprates in Bi-Ba-Ln-Cu-O systems. It depends on partial oxygen pressure and size of lanthanoid. Electronic states of variable valence atoms in layered cuprates with 2201 type structure differ from "usual" valence states.

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Liquid Crystal Dopant

Bull. Korean Chem. Soc. **1995**, Vol. 16, No. 6   489

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A New Synthesis of a Chiral Ester Containing Phenylpyrimidine Ring as Liquid Crystal Dopant

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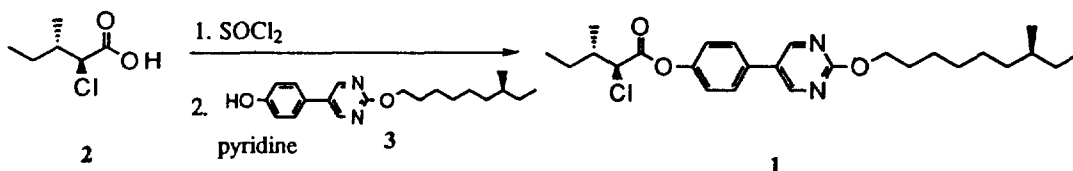*Received December 20, 1994*

A new synthetic route to chiral liquid crystal dopant, 4-[2-(7S-methylnonanyl)oxy-5-pyrimidinyl]phenyl (2S,3S)-2-chloro-3-methylpentanoate (1), starting from 4-nitrophenylacetic acid is described. The key intermediate methylthiopyrimidine compound (8) has been synthesized from 4-nitrophenylacetic acid by Vilsmyer-Haack reaction followed by the formation of pyrimidine ring, and then converted to chiral ester (1) by the replacement of nitro group by (2S,3S)-2-chloro-3-methylpentanoic acid 2 through the formation of diazonium salt.

Introduction

Recently, new liquid crystal display elements using a ferroelectric liquid crystal are actively studied because of their bistable and fast switching properties.[1] This liquid crystal display system utilizes a tilted smectic liquid-crystalline phases. if suitable chiral dopants are added to such tilted smectic phases, the phases can be transformed into a ferroelectric liquid crystalline phase.[2]

Accordingly, a lot of optically active dopants for ferroelec-

tric liquid crystals were synthesized for the development of fast response display devices.[3] Among them, a chiral ester (1) containing phenylpyrimidine ring is known as a suitable dopant for tilted smectic liquid-crystalline phases.[3c] However, prior report merely gives a conventional preparation process of 1 by the reaction of acid chloride derivative, derived from (2S,3S)-2-chloro-3-methylpentanoic acid 2, with pyrimidinyl-phenol derivative 3 without detailed experimental procedures as shown in Scheme 1.

Scheme 1