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Structure and Bonding of Perovskites $A(Cu_{1/3}Nb_{2/3})O_3$ (A=Sr, Ba and Pb) and Their Series of Mixed Perovskites

Hyu-Bum Park, Hwang Huh†, and Si-Joong Kim*

Department of Chemistry, Korea University, Seoul 136-701

†Department of Chemistry, Ul-San University, Ul-San 680-749. *Received July 29, 1991*

Some perovskites $A(Cu_{1/3}Nb_{2/3})O_3$ ($A=Sr^{2+}$, Ba^{2+} and Pb^{2+}) and their series of mixed perovskites have been prepared by solid state reaction. Single perovskite phase was obtained in Sr or Ba rich samples, but pyrochlore phase was found in Pb rich samples. The stability of perovskite phase is dependent on the ionicity of bonding as well as the tolerance factor. All the obtained perovskites have tetragonal symmetry distorted by Jahn-Teller effect of Cu^{2+}. In the case of $Sr(Cu_{1/3}Nb_{2/3})O_3$, some superlattice lines caused by threefold enlarging of fundamental unit cell were observed. And, the symmetry of B site octahedron and the bonding character of B-O bond have been studied by IR, ESR and diffuse reflection spectroscopy. It appeared that the symmetry and the bonding character are influenced by such factors as the size and the basicity of A cation.

Introduction

Many compounds with the general formula ABO_3 having perovskite structures have been prepared and studied by many investigators.[1-4] These compounds exhibit many interesting physical properties such as ferroelectricity, piezoelectricity, and larger variation in electric and magnetic behaviours.[5-8] These properties depend on not only the crystal

structure, but also the properties of A and B ions. In oxide perovskites, although the bonding character is predominantly ionic, there exists a secondary covalent bonding between B ion and oxide ion, and also the B ion interacts with A ion through oxide ion. The electric and magnetic properties are directly related to the bonding properties.[5,9] To understand the properties of perovskites, hence, it is necessary to know the interaction between A ion and B ion.

In this research, we carried out a detailed study to understand the influences of A site ion on the structure and the bonding character for the perovskites $A(Cu_{1/3}Nb_{2/3})O_3$ ($A=Sr^{2+}$, Ba^{2+} and Pb^{2+}) and their series of mixed perovskites by XRD, IR, ESR, and diffuse reflection spectroscopy.

Experimental

All samples were prepared by solid state reaction. Each sample was prepared by mixing $SrCO_3$, $BaCO_3$, PbO, Nb_2O_5 and $Cu(CH_3COO)_2 \cdot H_2O$ through ball milling. The mixed powders were reacted at 850-950℃ for 3 hr in alumina crucible and pressed into pellets, then further reacted at 950-1100℃ for 5-50 hr. Pellets containing PbO were covered with the same compositional powders to minimize PbO evaporation at a given synthetic condition. The compositions of the final samples were checked by X-ray energy dispersive spectroscopy.

The phases and the crystal structures of the obtained samples were identified by X-ray powder diffraction with Cu Kα radiation and the lattice parameters were calculated by Cohen's method. IR spectra were obtained in the range of 1000-400 cm^{-1} by employing BOMEM MB-100 spectrometer as KBr pellet. Diffuse reflection spectra of powdered samples were measured on Shimadzu UV-3100S spectrometer. To investigate the symmetry of CuO_6 and the covalency of Cu-O bond, ESR spectra were recorded in X-band frequency region by Bruker ER 200D-SRC at room temperature.

Results and Discussion

The perovskite (ABO_3) structure is regarded as close-packed AO_3 layers with B cations in octahedral holes. The A ions are coordinated by twelve oxide ions and B ions by six. In general, the stability of perovskite structure can primarily be estimated by geometrical consideration and described in terms of a tolerance factor, t, defined as

$$t=(r_A+r_O)//1.414\ (r_B+r_O)$$

where r_A, r_B and r_O are ionic radii of the respective ions. In an ideal cubic perovskite where the ions are just touching one another, the tolerance factor is unity. When the tolerance factor is around unity, the perovskite phase is stable. The tolerance factors calculated using Shannon's[10] ionic radii are close to 1.0[$Sr(Cu_{1/3}Nb_{2/3})O_3$ [SCN], $t=0.97$; $Ba(Cu_{1/3}Nb_{2/3})O_3$ [BCN], $t=1.03$; $Pb(Cu_{1/3}Nb_{2/3})O_3$ [PCN], $t=0.99$]. All the samples, therefore, are expected to form perovskite phases.

XRD. XRD patterns in Figure 1 show that SCN and BCN form single perovskite phases, but PCN is composed of $Pb_3Nb_4O_{13}$ (pyrochlore), PbO (yellow) and CuO (tenorite). It is well known that several Pb-based perovskites are difficult to prepare because of formation of pyrochlore phase.[11,13] From studies of formation of Pb-based perovskite, Halliyal and co-workers[11] have reported that an important factor to be considered in preparing those perovskites is the electronegativity difference between cation and anion, and that those Pb-based perovskites can be prepared by small addition of some other perovskites having higher ionicity. Since the difference of electronegativity in Pb-O is smaller than that in Sr-O and Ba-O, it would be difficult for the PCN composition to form perovskite phase. The XRD pattern of PCN can be analyzed as a result of the following reaction similar to that reported in the other papers.[12,13]

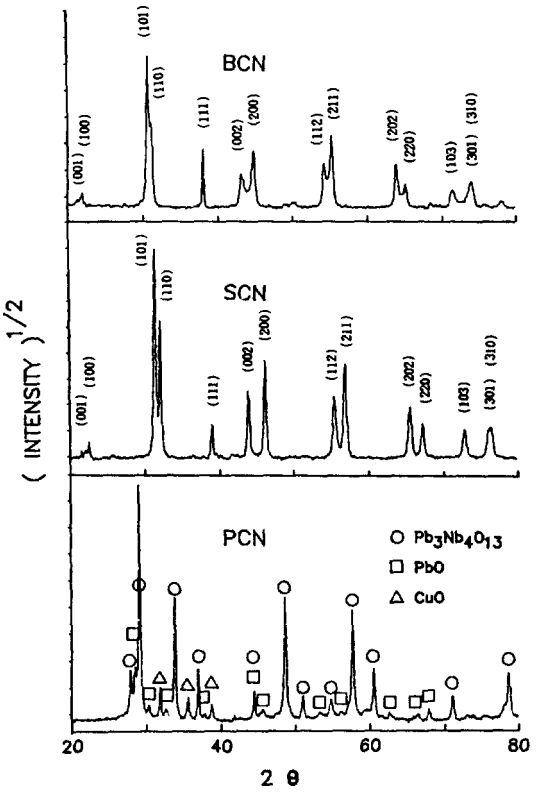

Figure 1. XRD patterns of $Ba(Cu_{1/3}Nb_{2/3})O_3$ (BCN), $Sr(Cu_{1/3}Nb_{2/3})O_3$ (SCN) and $Pb(Cu_{1/3}Nb_{2/3})O_3$ (PCN).

$$6PbO+2Nb_2O_5+2CuO \longrightarrow Pb_3Nb_4O_{13}+3PbO+2CuO$$

The XRD patterns of SCN and BCN show the tetragonal distortion of crystal lattice, and SCN especially shows larger distortion. It seems that the tetragonal distortion is caused by Jahn-Teller distortion of Cu^{2+} in BO_6 octahedron. In the case of SCN ($t=0.97$), small Sr^{2+} can cause co-operative buckling of the corner-shared octahedron which enlarges the unit cell,[14] and the buckling can distort the closed packing of ions in crystal lattice. The larger distortion in SCN would take place as a consequence of the buckling and it seems that this distortion would enhance the structural stability.

The phase diagrams of three systems, $(1-x)$BCN$-x$SCN, $(1-x)$PCN$-x$BCN, and $(1-x)$PCN$-x$SCN, are presented in Figure 2. The series $(1-x)$BCN$-x$SCN forms a complete solid solution of perovskite phase, but $(1-x)$PCN$-x$BCN and $(1-x)$PCN$-x$SCN do not form solid solution in the region of higher Pb^{2+} content with the formation of undesired pyrochlore ($Pb_3Nb_4O_{13}$). All the obtained perovskite phases are tetragonal due to the cooperative Jahn-Teller distortion of

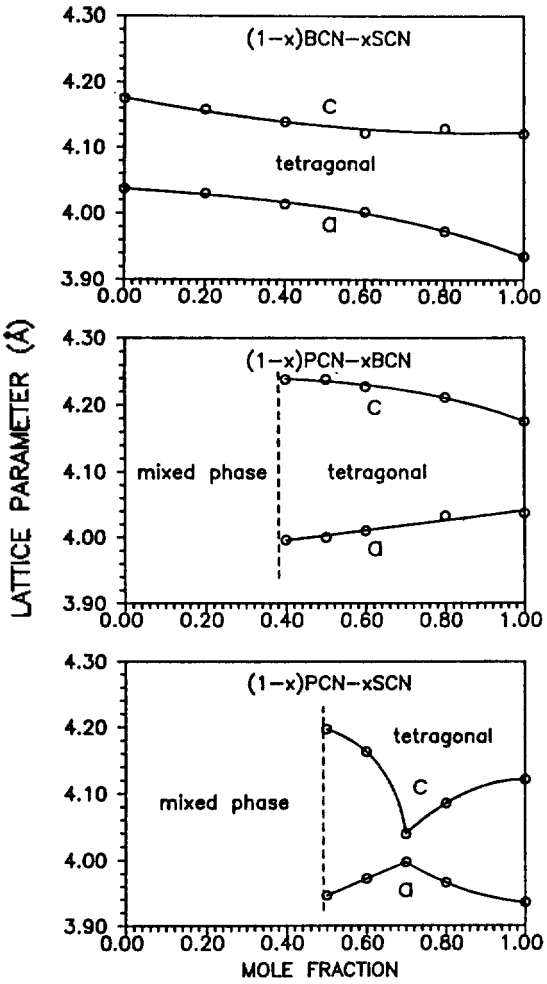

Figure 2. Phase diagrams of $(1-x)$BCN$-x$SCN, $(1-x)$PCN$-x$BCN and $(1-x)$PCN$-x$SCN.

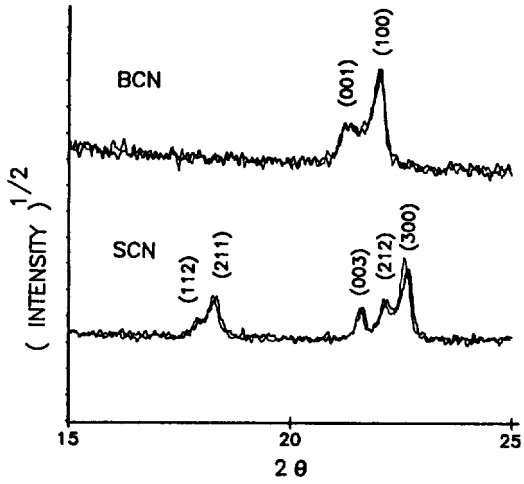

Figure 3. XRD patterns of SCN and BCN obtained by heat treatment at 1100℃ for 50 hr (thin line) and additional annealing at 800℃ for 15 hr (thick line).

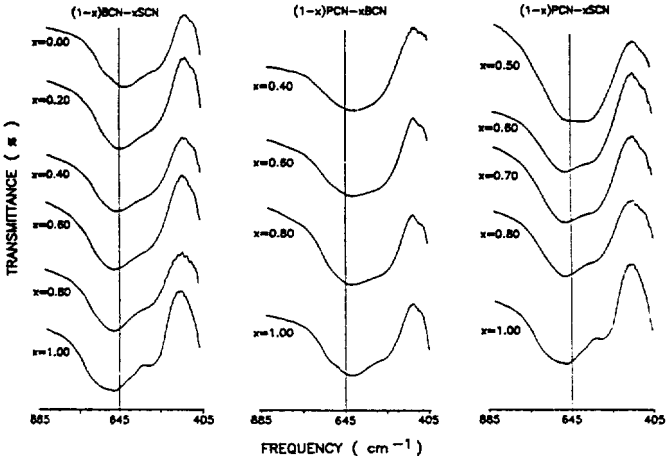

Figure 4. IR spectra of $(1-x)$BCN$-x$SCN, $(1-x)$PCN$-x$BCN and $(1-x)$PCN$-x$SCN.

Cu^{2+}, which might be an important factor determining the crystal symmetry. As Ba^{2+} of BCN is substituted for Pb^{2+}, the tetragonality is increased. This increase of tetragonality seems to be caused by inert pair effect of Pb^{2+}. In some compounds, the $6s^2$ electrons of Pb^{2+} are stereochemically active, since this electron pair is not in spherically symmetrical orbital but stick out to one side of the Pb^{2+} ion.[9] The inert pair is able to bring about a distortion of coordination polyhedra of the metal ion, furthermore, a distortion of the crystal structure.[9,15,16] Assuming that there is the inert pair effect, the tetragonal distortion in Pb^{2+} rich samples can be promoted by the addition of co-operative inert pair effect to Jahn-Teller effect. $(1-x)$PCN$-x$SCN series exhibits a point of lower tetragonality near $x=0.7$, which seems to be difficult to be interpreted. It is thought that another factor which does not exist in $(1-x)$BCN$-x$SCN and $(1-x)$PCN $-x$BCN may play an important role in $(1-x)$PCN$-x$SCN.

If there are more than one kind of ion in B site, the ordering of B site ions is possible. It has been known that the ordering of B ions is more probable when a large difference exists in size and charge between the B ions.[17,18] Superlattice lines of BCN and SCN were investigated for the samples reacted at 1100℃ and annealed at 800℃ to improve the ordering. In Figure 3, SCN shows some superlattice lines [(112), (211), and (212)] due to threefold enlarging of fundamental unit cell, but BCN does not show noticeable superlattice lines under the same X-ray diffraction condition. Since the A site is occupied entirely by Sr^{2+} and the B site is composed of two different ions ($1/2Cu^{2+}$ and $2/3Nb^{5+}$) in SCN, and the differences in charge and size between Cu^{2+} and Nb^{5+} are enough to cause an ordering, it can be suggested that the threefold enlarging of unit cell takes place as a result of the 1 : 2 ordering of B site ions (CuNbNbCuNbNb···).

IR Spectra. The vibrational spectra of perovskites have been frequently described as the internal vibration of the octahedron containing highly charged and small B ion because of relatively weak A-O bond.[19-21] In $A(Cu_{1/3}Nb_{2/3})O_3$ compounds, the Nb-O bonding is expected to be stronger and more covalent than the Cu-O bonding, and thus the NbO_6 group is regarded as a molecular unity. Blasse and Corsmit[22] have reported that the stretching frequencies of NbO_6 group for some perovskites are ranged between 590 and 660 cm^{-1}, and also Husson and co-workers[23] have repor-

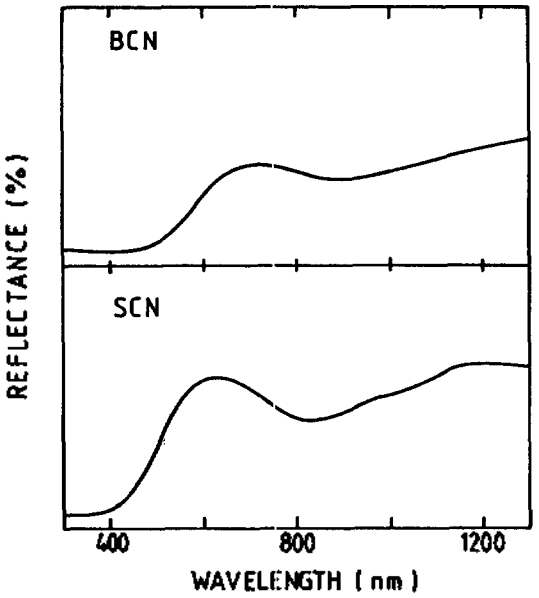

Figure 5. Diffuse reflection spectra of BCN and SCN.

ted that the stretching frequency of NbO_6 in $Pb(Mg_{1/3}Nb_{2/3})O_3$ is 600 cm^{-1}. In three series, IR absorptions are observed between 540 and 670 cm^{-1} (see Figure 4).

The BO_6 octahedron has 15 internal degrees of freedom or normal vibrations: $A_{1g}+E_g+2T_{1u}+T_{2g}+T_{2u}$. According to group theoretical consideration, the two T_{1u} modes are IR active and correspond to the stretching and the bending motions in BO_6 octahedron. Since the crystal symmetry for each sample is tetragonal, there is quite a possibility that the NbO_6 octahedron is tetragonally distorted. If O_h symmetry of NbO_6 is lowered to D_{4h}, it is expected that the T_{1u} modes are splitted into A_{2u} and E_u modes. The stretching motions corresponding to E_u are the vibrations of shorter Nb-O bonds in elongated octahedron, and that corresponding to A_{2u} is the vibration of longer Nb-O bond. Most of IR spectra in Figure 4 virtually show strong bands (E_u) around 650 cm^{-1} and shoulders (A_{2u}) at lower frequencies.

In $(1-x)$BCN$-x$SCN, the stretching frequency of Nb-O bond increases gradually from $x=0.00$ to 1.00. This increase may be ascribed to the size effect of A site ion. Small Sr^{2+} compresses the B site octahedron and thus the B-O bond length is shortened. Therefore, the gradual substitution of Sr^{2+} for Ba^{2+} of BCN results in the increase of stretching frequency. The IR spectrum of SCN shows the largest band splitting, which indicates the most distorted NbO_6 octahedron. The splitting degree between maximum (E_u) and shoulder (A_{2u}) increases with increasing Sr^{2+} content. This increase of band splitting is in good agreement with the increase of tetragonal distortion of crystal lattice observed by XRD.

IR sepectra of $(1-x)$PCN$-x$BCN and $(1-x)$PCN$-x$SCN show only a small shift of the stretching band of Nb-O. But, the IR bands of $(1-x)$PCN$-x$SCN are positioned at higher frequencies than those of $(1-x)$PCN$-x$BCN, which implies that the size of A site ion has an important effect on the B-O bond strength. In $(1-x)$PCN$-x$BCN, the splitting degree of IR bands decreases with increasing Pb^{2+} content, even though the tetragonality of unit cell increases. In addition, the band splitting in IR spectra continuously decreases with increasing Pb^{2+} content, although the phase diagram of $(1-x)$PCN$-x$SCN shows a minimum point of tetragonality near $x=0.70$. From these results, it turns out that the symmetry of NbO_6 is independent of the crystal symmetry in Pb^{2+} rich region and the behavior of Pb^{2+} in these perovskites is different from that of Sr^{2+} or Ba^{2+}.

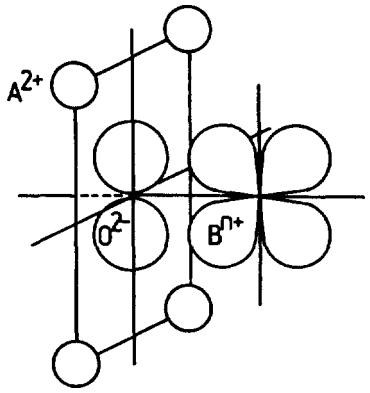

Figure 6. Anion coordination in perovskite structure.

Diffuse Reflection Spectra. Diffuse reflection spectra were measured to know variation of the band gap in compounds and the *d-d* transition energy of Cu^{2+}. It is well known that the magnitude of band gap depends on ionicity of bonding in solid.[9] Representative diffuse reflection spectra of BCN and SCN are shown in Figure 5. Absorption edges, which are designated as the wavelength having maximum derivatives of reflectance, are positioned at 510 nm for SCN and at 577 nm for BCN. Absorptions due to *d-d* transition of Cu^{2+} are also observed at 830 nm (and near 1000 nm as shoulder) for SCN and at 895 nm for BCN. SCN shows typical spectrum of Cu^{2+} ion in elongated octahedral field, but BCN does not show any remarkable shoulder.

It is assumed that the absorption edges observed in the range of 510-660 nm are due to absorption of niobate group and are originated from charge transfer transition in which an electron is transferred from the highest filled molecular orbital (localized on the oxide ions) to the lowest empty molecular orbital (localized on the niobium ion). In perovskite structure, the oxide ions are coordinated by B ions and by a square of four A ions at larger distances, this square being perpendicular to the collinear array B-O-B'[24] (see Figure 6). The occupied oxygen 2*p* orbitals are situated in the square composed of four A site ions and the empty t_{2g} orbital of Nb^{5+} is coordinated to the 2*p* orbital of oxide ion. Hence, by considering the fact that the 2*p* orbital can be directed toward A site ions, it is resonable for the absorption edge to depend on A site ion.

Figure 7 illustrates that the absorption edge depends on the composition of A site. In $(1-x)$BCN$-x$SCN series, the absorption edge decreases with increasing Ba^{2+} content in A site and the two systems containing Pb^{2+} also show the decrease of absorption edge with increasing Pb^{2+} content. The trend of absorption edge energy is, on the whole, Pb <Ba<Sr. This trend is reverse to the basicity of A site ions. If the A ion is able to give more electron cloud to oxide ion, the Nb-O bond becomes more covalent and the charge

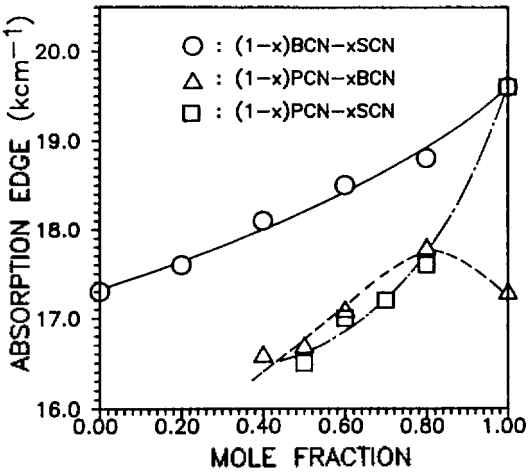

Figure 7. Variation of absorption edges for $(1-x)$BCN$-x$SCN, $(1-x)$PCN$-x$BCN and $(1-x)$PCN$-x$SCN.

transfer transition from O^{2-} to Nb^{5+} can be facilitated. More basic Pb^{2+} ion, therefore, shifts absorption edge to lower frequency.

ESR Spectra. ESR spectra were recorded to observe the symmetry of CuO_6 and the covalency in Cu-O bonding. All the obtained ESR spectra showed nearly isotropic shapes, which revealed symmetrical surroundings of Cu^{2+}, with the exception of SCN. The anisotropy of SCN seems to be ascribed to the lower symmetry caused by larger Jahn-Teller distortion. In IR spectrum of SCN, the largest band splitting is also observed. Therefore, it may be inferred that in the case of SCN both Cu^{2+} and Nb^{5+} have more distorted surroundings. The g gactors of three series are ranged in 2.20-2.15 (Table 1), which agree to the value 2.192 reported by Coffman[25] for Cu^{2+} doped MgO.

In $(1-x)$BCN$-x$SCN, the variation of g factor for Cu-O bonding is relatively small. The Cu-O in SCN is more covalent than that in BCN, which can be explained by the buckling effect. The CuO_6 octahedron is more compressed by smaller Sr^{2+}, and thus the orbitals between Cu^{2+} and O^{2-} is much more overlapped. However, the g factor in $(1-x)$PCN$-x$BCN series largely decreases with the increase of Pb^{2+} content. Pb^{2+} favors covalent bonding than Ba^{2+} ion and can give more electron cloud to oxygen ions and thus the covalency of Cu-O might be increased as the increase

Table 1. g Factor and ΔH_{pp}(G), of $(1-x)$BCN$-x$SCB, of $(1-x)$PCN$-x$BCN at Room Temperature

x	$(1-x)$BCN$-x$SCN		$(1-x)$PCN$-x$BCN		$(1-x)$PCN$-x$SCN	
	g	ΔH_{pp}	g	ΔH_{pp}	g	ΔH_{pp}
0.00	2.20	325	–	–	–	–
0.20	2.20	285	–	–	–	–
0.40	2.20	270	2.15	645	–	–
0.50	–	–	2.16	579	2.17	610
0.60	2.20	260	2.16	475	2.18	520
0.70	–	–	–	–	2.19	395
0.80	2.19	265	2.18	390	2.19	335
1.00	2.18	260	2.20	325	2.18	260

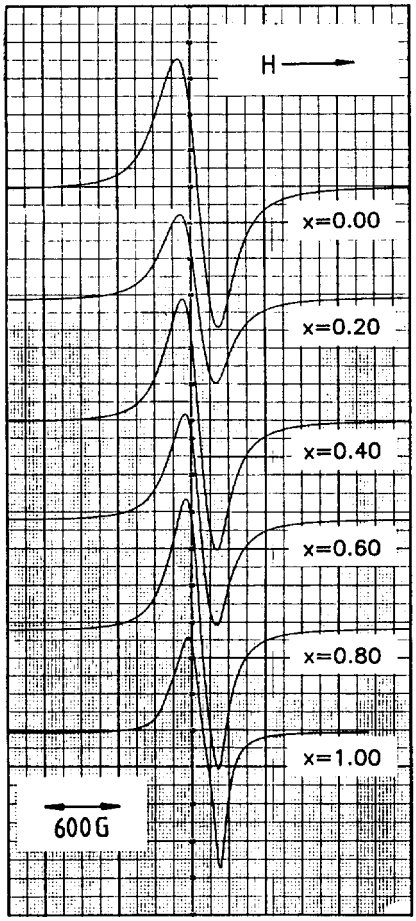

Figure 8. X-band ESR spetra of $(1-x)$BCN$-x$SCN at room temperature.

of Pb^{2+} content. The effect of basicity of Pb^{2+} on the increase of covalency of Cu-O is stronger than that of the buckling of Sr^{2+}. On the other hand, in $(1-x)$PCN$-x$SCN system a small decrease of g factor was observed. The buckling effect is reduced with increasing Pb^{2+} content, since Pb^{2+} (1.49 Å) is larger than Sr^{2+} (1.44 Å). In $(1-x)$PCN$-x$SCN, the effect of basic Pb^{2+} on g factor might be compensated by the reduced buckling.

By considering peak-to-peak linewidth (ΔH_{pp}) values tabulated in Table 1, the ΔH_{pp} considerably increases along with the decrease of g factor, as the Pb^{2+} content in A site increases. Such a phenomena could be explained by the enhancement of electron delocalization in the Cu-O bond due to the increment of covalency.

Conclusions

The stability of perovskite phase is related to both the tolerance factor and the difference of electronegativity between cation and anion in compound. All the crystal symmetry of obtained perovskites were tetragonal. The main factors determining crystal symmetry are Jahn-Teller distortion of Cu^{2+} and inert pair effect of Pb^{2+}. In SCN, some superlattice lines cuased by three fold enlarging of unit cell were observed.

The stretching frequency of Nb-O bond depended on the

size of A ion and the symmetry of NbO_6 on both the crystal symmetry and the property of A ion. The absorption edge decreased, as the basicity of A ion was increased and the size of A ion was decreased. ESR spectra of Cu^{2+} showed nearly isotropic shapes with the exception of SCN and the covalency of Cu-O bond depended on the basity and the size of A ion. The important factors, which affect the bonding character of B-O and the symmetry of BO_6 octahedron, were the size ad the basicity of A ion.

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Infrared Spectra and Electrical Conductivity of The Solid Solutions $X\ MgO+(1-X)\ \alpha-Nb_2O_5$; $0.01 \leq X \leq 0.09$

Zin Park, Jong Sik Park, Dong Hoon Lee, Jong Ho Jun†, Chul Hyun Yo, and Keu Hong Kim*

Department of Chemistry, Yonsei University, Seoul 120-749
†Department of Biochemistry, Kon-Kuk University, Chungju 380. *Received August 10, 1991*

Changes in network structures of α-Nb_2O_5 in the $X\ MgO+(1-X)$ α-Nb_2O_5 solid solutions occurring as the MgO doping level (X) was varied were investigated by means of infrared spectroscopy and X-ray analysis. X-ray diffraction revealed that all the synthesized specimens have the monoclinic structure. The FT-IR spectroscopy showed that the system investigated forms the solid solutions in which Mg^{2+} ions occupy the octahedral sites in parent crystal lattice. Electrical conductivities were measured as a function of temperature from 600 to 1050℃ and P_{O_2} form 1×10^{-5} to 2×10^{-1} atm. The defect structure and conduction mechanism were deduced from the results. The 1/n value in $\sigma \propto P_{O_2}^{1/n}$ is found to be $-1/4$ with single possible defect model. From the activation energy (E_a=1.67-1.73 eV) and the $1/n$ value, electronic conduction mechanism is suggested with a doubly charged oxygen vacancy.

Introduction

The polymorphism of niobium pentoxide has been studied by several investigators. The α form of Nb_2O_5 is the most thermodynamically stable polymorph in the high temperature. The transition temperature of the α form from the low temperature modification has been found to be approximately 830℃ and the transition is irreversible[1]. The structure of α-Nb_2O_5 is derived from the ReO_3-type structure. The crystal structure of α-Nb_2O_5 has been found to be monoclinc, space