

SOLID SOLUTION AND DEFECT STRUCTURE OF LiCrO_2 IN THE PSEUDO-BINARY JOINS: $\text{LiCrO}_2\text{-MgCr}_2\text{O}_4$ AND $\text{LiCrO}_2\text{-MgAl}_2\text{O}_4$

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ABSTRACT

In the system of $\text{Li}_2\text{O-MgO-Al}_2\text{O}_3\text{-Cr}_2\text{O}_3$, the crystalline solid solution of LiCrO_2 along the Pseudo-binary join between rocksalt structure(LiCrO_2) and spinel structure(MgCr_2O_4 or MgAl_2O_4) have been investigated by X-ray diffraction techniques. In this study, order-disorder phase transition of LiCrO_2 was observed and the unit cell of the disordered LiCrO_2 structure has been established. It has been found that LiCrO_2 made a solid solution over a wide range with MgAl_2O_4 , while not with MgCr_2O_4 . This difference was explained as being due to the ability of oxygen lattice distortion which depend on relative sizes and chemical bonding characteristics of the substituted ions.

INTRODUCTION

Solid solutions are of great practical importance, because they provide fairly predicable means of modifying physical properties for desire. For the solid solutions in the non-metallic systems, very little theoretical progress has been achieved and many fundamental questions remain.

It is well known quantitative four-factors to affect extensive solid solubility [1,2] : (1) size factor (2) valency factor (3) chemical affinity and (4) structure type. With these factors, however, for a given system it is usually impossible to predict whether solid solubility will be formed or not, if they are

formed, what is their compositional extent. Instead, this has to be determined experimentally.

Since the ligand field theory was successfully applied to interpret various coordination metal ions [3, 4, 5], it has played an important role in explaining some principles of crystal structure such as coordination, stabilization of atoms, and various physical properties.

The numerous studies for the type LiMO_2 , where M denotes a trivalent first row transition metal, has made for the structure and related physical properties [6, 7, 8, 9, 10]. The structure types occurring in this series are all derived from that of sodium chloride.

In this study, order-disorder phase transitions of LiCrO_2 and crystalline solid solution between LiCrO_2 (rocksalt str.) and MgCr_2O_4 or MgAl_2O_4 (spinel str.) were investigated. And here special attention is paid to relations of the defect-induced lattice stress and distortion in the host matrix, LiCrO_2 with ligand field interaction.

EXPERIMENTAL PROCEDURE

MgAl_2O_4 , MgCr_2O_4 , LiCrO_2 were taken as end members in $\text{Li}_2\text{O-MgO-Al}_2\text{O}_3\text{-Cr}_2\text{O}_3$ system. Fig. 1 shows these systems. Excepting $\text{Al}_2\text{O}_3\text{-MgCr}_2\text{O}_4$ system formed complete solid solution [11, 12], the systems $\text{LiCrO}_2\text{-MgAl}_2\text{O}_4$ and $\text{LiCrO}_2\text{-MgCr}_2\text{O}_4$ were studied with compositional change.

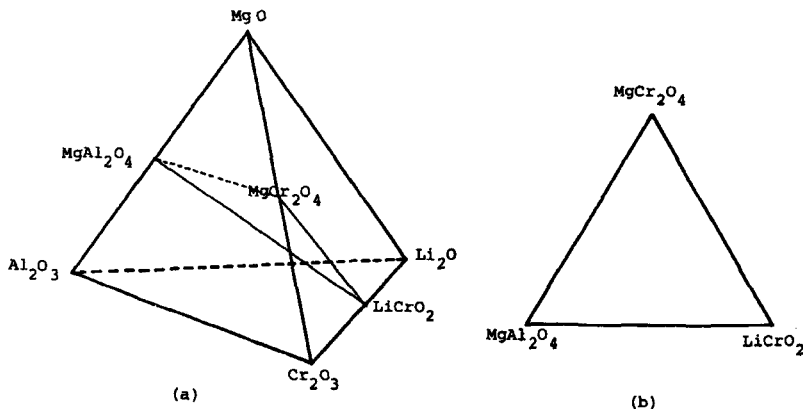


Fig. 1 System of (a) $\text{Li}_2\text{O-MgO-Al}_2\text{O}_3\text{-Cr}_2\text{O}_3$ and (b) pseudo-binary system

Powders of precisely determined chemical composition (Table 1) were mixed with acetone and calcined at 800°C for 2 hours. The calcined materials were thoroughly reground, and then pressed into disks.

These pressed bodies were fired at 1,200–1,500°C for 1–6 hours with compositional variation and cooled down slowly at 1,200°C and then air quenched. Especially the order–disorder experiment of LiCrO_2 was conducted at 1000–1200°C for 3 hours to reaction and then air quenched.

The phases and lattice parameters of prepared samples were determined by powder X-ray diffraction (Rigaku, D/MAX) and also microstructures were examined by SEM and EDAX (Akashi, DS-130).

RESULTS AND DISCUSSION

Phase Transition of LiCrO_2

It was reported that LiCrO_2 has ordered rocksalt structure with space group $R\bar{3}m$ [13] as shown in Fig. 2. In this study, however, order–disorder phase transition was found at the temperature range 1100°C to 1150°C. Fig. 3 shows X-ray diffraction patterns of LiCrO_2 air quenched at 1100°C and 1150°C. The X-ray patterns of

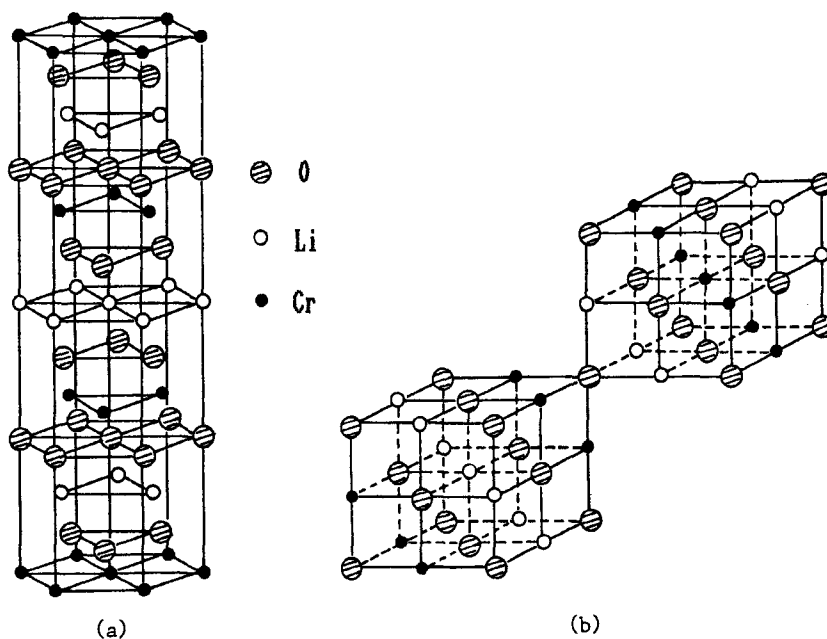


Fig. 2 Crystal structure of LiCrO_2 (a) hexagonal viewpoint
(b) cubic viewpoint

air quenched sample at 1100°C [Fig.3(a)] represent ordered LiCrO_2 as same as patterns reported by Tauber[13], its unit cell as hexagonal viewpoint ($a=2.902\text{\AA}$, $c=14.42\text{\AA}$) is shown in Fig.2 (a). The sequence of layers of the ordered structure is---ABCBACB--- along the C-axis. In ordered LiCrO_2 , the diffraction intensity(I/I_0) of (003) plane composed by Cr^{3+} layers is 100 and this come from much greater scattering factor of Cr^{3+} than Li^+ or O^{2-} .

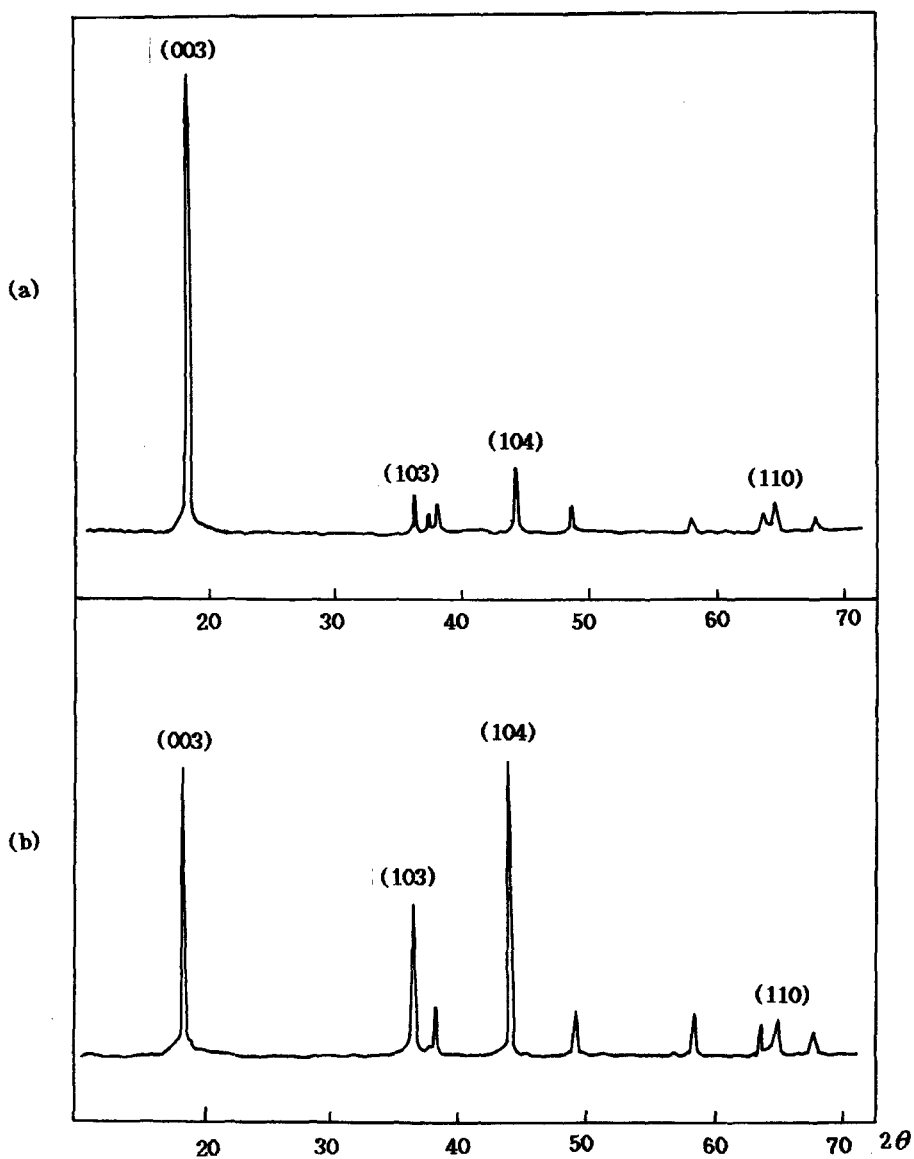


Fig.3 X-ray diffraction patterns of LiCrO_2 heat treated at (a) 1100°C and (b) 1150°C

However, the X-ray pattern(Fig. 3(b)) of LiCrO_2 air quenched above 1150°C shows different result that the intensity of (003) plane is lowerd 100 to 97 and the intensity of (104) plane is increased 14 to 100. This variation of intensity means that the rearrangement of Li^+ and Cr^{3+} ions which have the greatest scattering factor. The order-disorder transition arise from cation rearrangement as entropy to be dominated with temperature increase without anion rearrangement. In the case of disordering of LiCrO_2 , the (003) plane which is composed only Cr^{3+} ions in ordering irregularly rearranged with Cr^{3+} and Li^{2+} ions. As a result, the intensity of (003) plane is relatively lowered and that of the other planes is increased. The disordered LiCrO_2 structure to be established in this study is shown in Fig. 4 ($a=2.899\text{\AA}$, $c=7.23\text{\AA}$) and there are no change in symmetry and space group; $R\bar{3}m$.

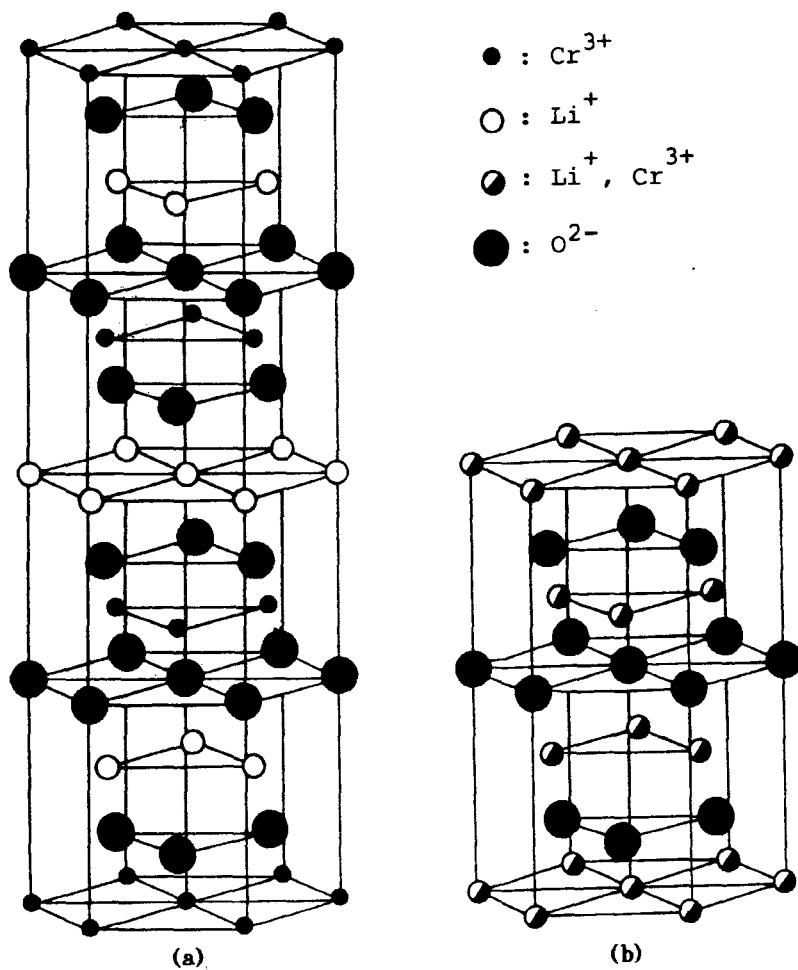
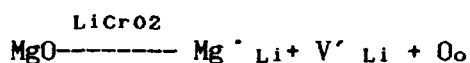


Fig. 4 Unit cell of LiCrO_2
(a) ordered(1100°C) and (b) disordered(1150°C)

The order-disorder transition of LiCrO_3 is observed between 1000°C and 1150°C but further work is necessary to fully understand the nature of this disordered structure.

Solid solubility of LiCrO_2 in $\text{LiCrO}_2\text{-MgCr}_2\text{O}_4$ join

In $\text{LiCrO}_2\text{-MgCr}_2\text{O}_4$ system, when postulating the substitution of Li^+ with Mg^{2+} , the reaction will be given by



However, there are no changes in lattice parameter in the $\text{LiCrO}_2\text{-MgCr}_2\text{O}_4$ system shown in Fig 5. In order to understand this result, a study for relations of lattice distortion and metal-oxygen bond nature is needed.

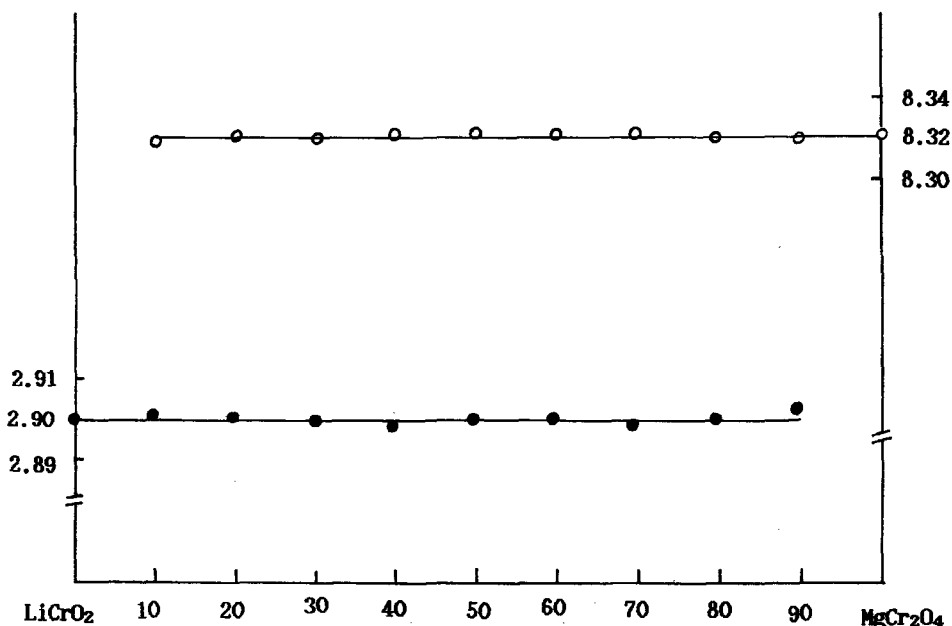


Fig. 5 The variation of lattice parameter for 'a' axis of LiCrO_2 and MgCr_2O_4 phase in $\text{LiCrO}_2\text{-MgCr}_2\text{O}_4$ system

Ligand field theory was applied with considerable success to the interpretation of spectroscopic, thermodynamic and stereo-chemical data on discrete transition metal complexes. This fundamental basis of theory has been extended to take into account the effect of covalent bonding in addition to the purely electrostatic effect of the environment. This theory is also

applicable to such solid as transition metal oxides.

The result in Fig. 5 come from ligand field stabilization of Cr^{3+} ion. The octahedral hybrid (d^2sp^3) orbitals occur in the transition elements which have partially filled d shells[14]. In this case, six bonds is directed toward the centers of six faces of a cube and the steric constraints will permit covalent bonds to stabilize the cation. All six octahedrally directed bonds are partially covalent, partially ionic. This contributions of partially covalent bonding of Cr^{3+} ion have their own bonding characters of symmetry and geometry which may have strong influence on the lattice distortion in a crystal matrix with resisting any distortion of the octahedral bond angles and length. In this way the resistance to distortion of regular octahedral symmetry of Cr^{3+} ion ligand can act to keep ligand anions from shifting there position. Cr^{3+} ion is most effectively stabilized in the octahedral site by ligand field interaction in the oxide matrix. Following shows excess octahedral stabilization energies[15]

Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Ti^{3+}	V^{3+}	Cr^{3+}	Mn^{3+}
17	31	86	64	29	54	158	95

Fig.6 shows the scheme of this bonding manner. To distinguish bonding character, two kind of bridge lines are used, thick bold line represents strong covalent bond nature for $\text{Cr}^{3+}-\text{O}^{2-}$ bonds, and dotted line, ionic bond nature for $\text{Li}^{+}-\text{O}^{2-}$ bond. Supposing substitution of Li^{+} ion with Mg^{2+} ion, Mg^{2+} size difference between $\text{Mg}^{2+}(0.65\text{\AA})$ and $\text{Li}^{+}(0.60\text{\AA})$ ions may induced some internal stress in the lattice[16]. Consequently, for further accommodation of Mg^{2+} in the Li^{+} sites, the effective lattice strain should be accompanied with the relaxation of lattice internal stress. For bond relations, all oxygen ions are participated in the ligands of Cr^{3+} ions with symmetry restricted covalence. In consequence, internal stress field can not be effectively relaxed for accommodation of Mg^{2+} ion in the LiCrO_2 lattice.

Therefore it is thought that solid solubility $\text{LiCrO}_2\text{-MgCr}_2\text{O}_4$ join was negligible. Fig.7 shows SEM of sintered specimens in $\text{LiCrO}_2\text{-MgCr}_2\text{O}_4$ join and (a) represents pure LiCrO_2 particle and (b),(c),(d) show microstructure with variation of mole ratio. It seems that small particle is MgCr_2O_4 and large particle is LiCrO_2 in Fig.7 (b),(c),(d), because Mg-peak is founded only at small particles in EDAX analysis(Fig.8). This result is also assured by increase of small particle with increase of MgCr_2O_4 mole ratio.

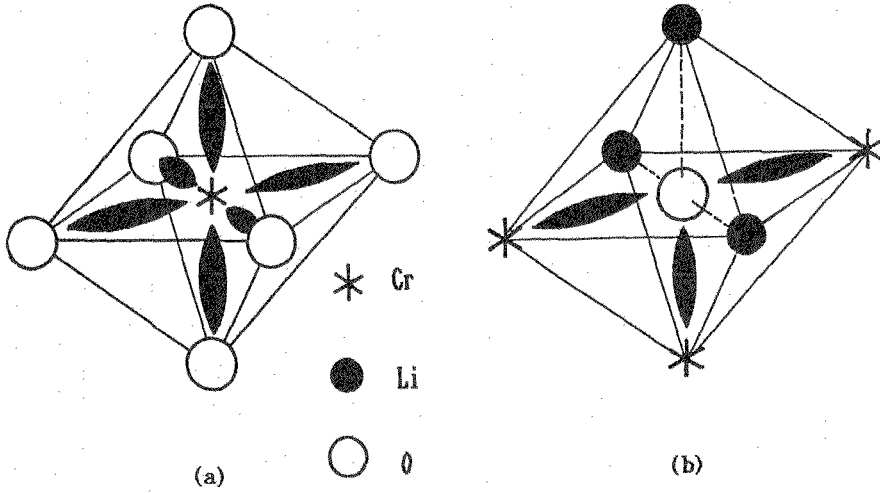


Fig. 6 Bonding manners of Cr^{3+} and O^{2-} ions environment in LiCrO_2 (a) Cr^{3+} ion center octahedron (b) O^{2-} ion center octahedron

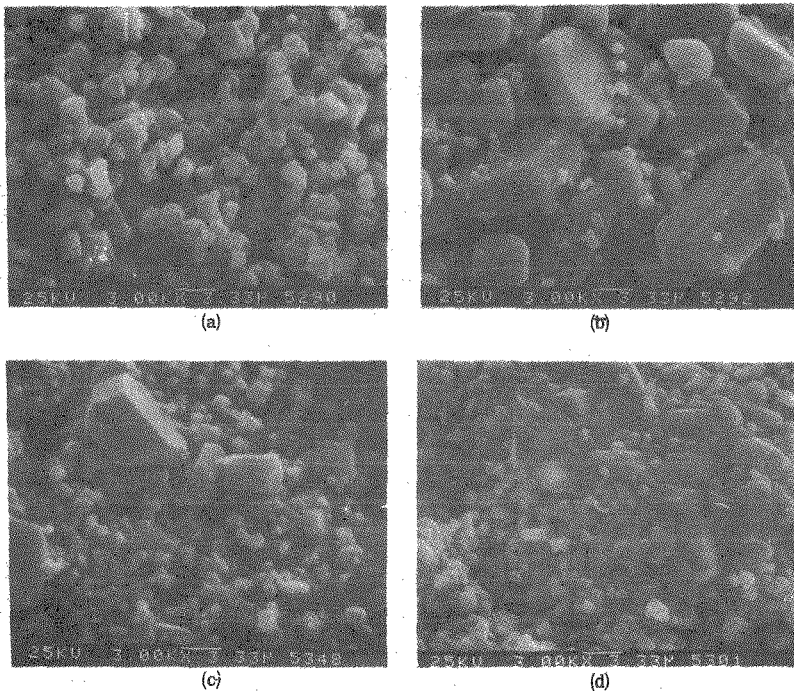


Fig. 7 SEM photos of the sintered specimen in $\text{LiCrO}_2\text{-MgCr}_2\text{O}_4$ join (a) LiCrO_2 (b) $0.8 \cdot \text{LiCrO}_2\text{-}0.2 \cdot \text{MgCr}_2\text{O}_4$ (c) $0.4 \cdot \text{LiCrO}_2\text{-}0.6 \cdot \text{MgCr}_2\text{O}_4$ (d) $0.2 \cdot \text{LiCrO}_2\text{-}0.8 \cdot \text{MgCr}_2\text{O}_4$

Table 1. Raw Materials

Material	Purity(%)	Supplier
Li ₂ CO ₃	99.997	Aldrich Chem. Com.
MgO	99.99	Aldrich Chem. Com.
Al ₂ O ₃	99.99	Sumitomo Chem. Com.
Cr ₂ O ₃	99.8	Avondale Lab.

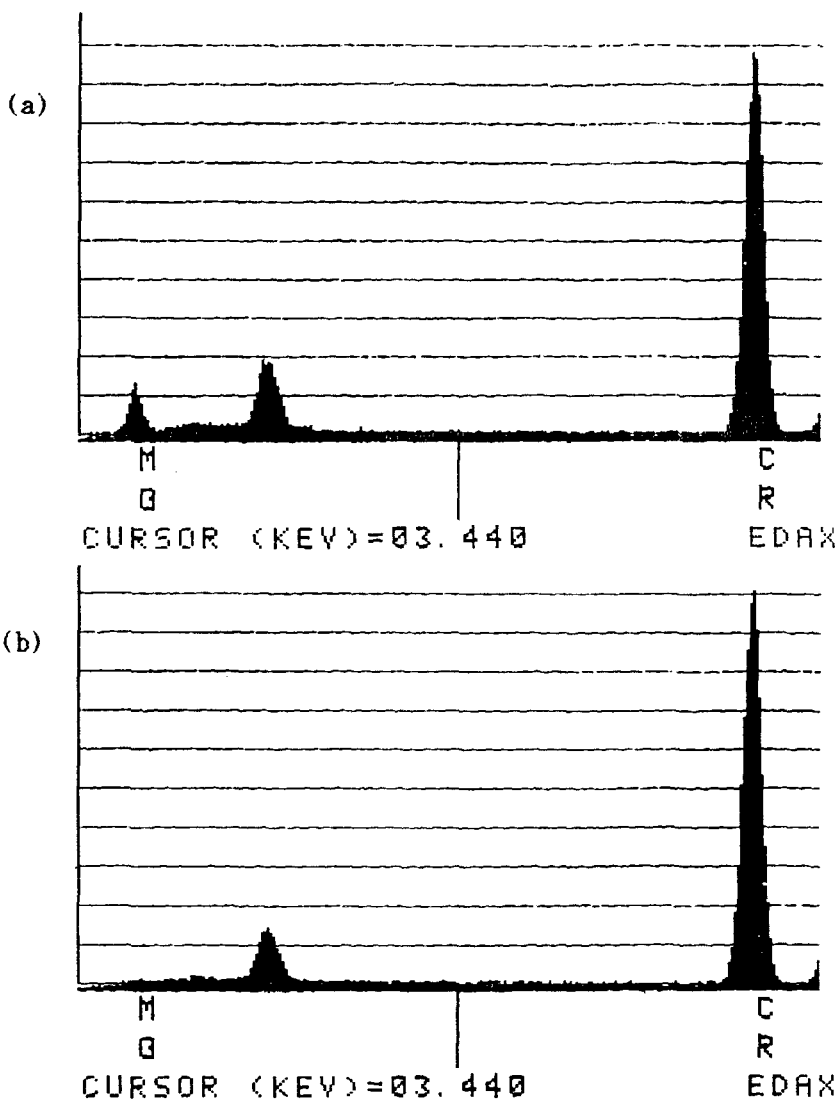
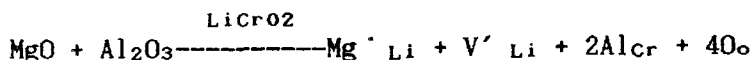


Fig. 8 EDAX results of (a) small particles
and (b) large particles

Solid solubility LiCrO_2 in $\text{LiCrO}_2\text{-MgAl}_2\text{O}_4$ Join

In $\text{LiCrO}_2\text{-MgAl}_2\text{O}_4$ system when Li^+ and Cr^{3+} ions of LiCrO_2 are substituted with Mg^{2+} and Al^{3+} ions, following reaction is assumed



Concerning size misfit relation, size difference between host and impurity ions will cause local lattice strain by expansion or contraction. The defect of Al_{Cr} , which is easily expected from $(\text{Al},\text{Cr})_2\text{O}_3$ (14,15) or $\text{Mg}(\text{Al},\text{Cr})_2\text{O}_4$ (16,17) series, leads to site size contraction since size difference, $r_{\text{Al}^{3+}} < r_{\text{Cr}^{3+}}$, and vacancy, V'_{Li} , also produces site contraction. The formation of Mg'_{Li} defect needs the lattice site size adjustment by position displacement of neighboring oxygen ions. In this case of $\text{LiCrO}_2\text{-MgAl}_2\text{O}_4$ series, it is supposed that lattice strain of LiCrO_2 can be happened in different way from that of $\text{LiCrO}_2\text{-MgAl}_2\text{O}_4$ series. From the bond nature view point the substitution of Cr^{3+} with Al^{3+} ion, Al_{Cr} , causes to change metal-oxygen bonding characters which deeply affect the type of lattice framework, by the effective elimination of central hard ion(Fig.9). This variation of oxygen environmental bond nature may give more feasibility of the displacement of O^{2-} ion by which size modification of cation sites makes possible in a lattice. This may lead to the higher probability of oxygen sublattice distortion needed for adjusting the charge of lattice condition with various defect formation. Consequently, it is expected that the appropriate site for Mg^{2+} ion will be more easily assured in the LiCrO_2 matrix of $\text{LiCrO}_2\text{-MgAl}_2\text{O}_4$ system comparing with those of $\text{LiCrO}_2\text{-LiMg}_2\text{O}_4$ system in which any replacement of Cr^{3+} ions could not occur. And the relaxation of internal stress at Mg'_{Li} sites due to size misfit can be progressed with the effective lattice strain for further accommodation of Mg^{2+} ion.

Therefore in the $\text{LiCrO}_2\text{-MgAl}_2\text{O}_4$ system the solubility of LiCrO_2 resulted in wide range. Fig.10 shows the variation of lattice parameters of solid solution of LiCrO_2 in $\text{LiCrO}_2\text{-MgAl}_2\text{O}_4$ join determined by X-ray analysis. In this figure, the increase in lattice parameter from 10 mol% MgAl_2O_4 result from governing of size contraction term by substitution of Cr^{3+} with small Al^{3+} ion and formation of lithium vacancy[17], rather than size increase term by substitution of Li^+ with large Mg^{2+} governing up to 10 mol% MgAl_2O_4 .

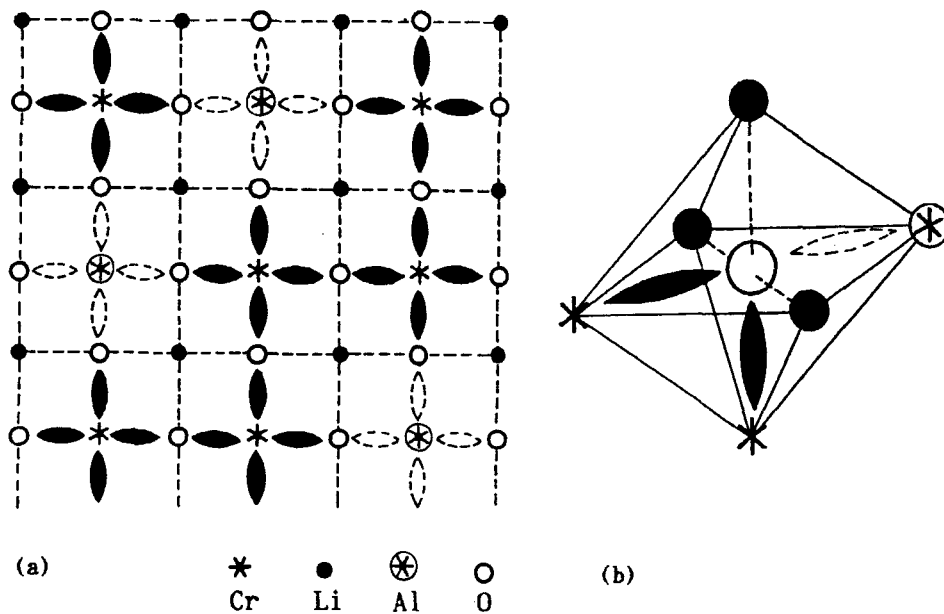


Fig. 9 Variation of bonding manner in $\text{LiCrO}_2\text{-MgAl}_2\text{O}_4$ system
 (a) 2-dimensional viewpoint (b) 3-dimensional viewpoint

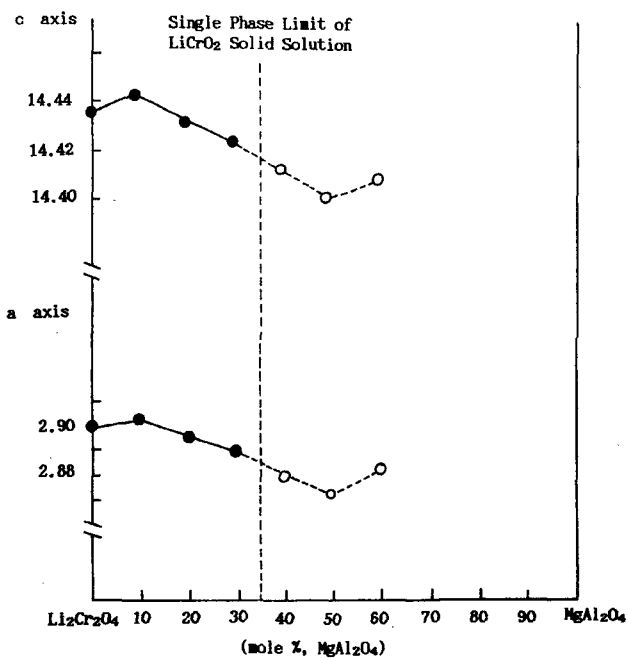


Fig. 10 Variation of lattice parameters of LiCrO_2 solid solution in $\text{LiCrO}_2\text{-MgAl}_2\text{O}_4$ join

CONCLUSION

The relationship between the stabilized d^2sp^3 ligand of Cr^{3+} ions with O^{2-} ions formed in crystal lattice and the site distortion of the oxygen framework was introduced to understand the mechanism of the solid solubility occurred in two pseudo-binary system, $(Li,Mg)(Cr,Al)_2O_4$ and $(Li,Mg)CrO_2$. In $LiCrO_2$ - $LiMg_2O_4$ series, Cr^{3+} ions make strong ligand with surrounding oxygen ions by localized hybridization and result in effect of fixing oxygen ions, therefore, somewhat large Mg^{2+} ion is not solved in $LiCrO_2$. In the case of $LiCrO_2$ - $MgAl_2O_4$ system having wide range solid solubility, however, substitution of Cr^{3+} with Al^{3+} has the effect of removing ligand and then induced easy displacement of oxygen ion which is an important factor in the formation of $LiCrO_2$ solid solution. It was also observed that order-disorder phase transition of $LiCrO_2$ took place between $1100^\circ C$ and $1150^\circ C$, and the unit cell of the disordered $LiCrO_2$ structure has been established.

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