

# Determination of Ionic Valency Pairs via Lattice Constants in Ordered Perovskites $(A\text{La})(\text{Mn}^{2+}\text{Mo}^{5+})\text{O}_6$ ( $A = \text{Ba}, \text{Sr}, \text{Ca}$ ) with Applications to $(A\text{La})(\text{Fe}^{3+}\text{Mo}^{4+})\text{O}_6$ , $\text{Ba}_2(\text{Bi}^{3+}\text{Bi}^{5+})\text{O}_6$ and $\text{Ba}_2(\text{Bi}^{3+}\text{Sb}^{5+})\text{O}_6$

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Assuming the lattice constants of perovskite-type compounds  $(AA')(BB')\text{O}_6$  where  $(AA' = \text{BaLa}, \text{SrLa}, \text{CaLa})$  to be a linear function of the ionic radii of  $B$  and  $B'$  ions, the ordered valency pair  $(\text{Mn}^{2+}\text{Mo}^{5+})$  in  $(AA')(\text{MnMo})\text{O}_6$  was verified from the lattice constants of a series of compounds  $(AA')(BB')\text{O}_6$  with known valency pairs  $(B, B') = (\text{Mn}^{2+}\text{Ta}^{5+}), (\text{Ta}^{5+}\text{Mg}^{2+}),$  and  $(\text{Mg}^{2+}\text{Mo}^{5+})$ . This method further elucidated the ordered pairs  $(\text{Bi}^{3+}\text{Bi}^{5+})$  in  $\text{BaBiO}_3$  and  $(\text{Bi}^{3+}\text{Sb}^{5+})$  in  $\text{Ba}_2(\text{BiSb})\text{O}_6$ , and a disordered pair  $(\text{Fe}^{3+}\text{Mo}^{4+})$  in  $(AA')(\text{FeMo})\text{O}_6$  where  $(AA' = \text{BaLa}, \text{SrLa})$ .

Ferrimagnetic behavior and a chemical shift of the fluorescent X-ray Mn-K $\beta$  line supported the valency pair  $(\text{Mn}^{2+}\text{Mo}^{5+})$  in  $(\text{SrLa})(\text{MnMo})\text{O}_6$ . The isomer shifts of Fe in Mössbauer absorption spectra and a random distribution of Fe and Mo from X-ray powder diffraction patterns supported the valency pair  $(\text{Fe}^{3+}\text{Mo}^{4+})$  in  $(AA')(\text{FeMo})\text{O}_6$  where  $(AA' = \text{BaLa}, \text{SrLa})$ . Eleven compounds were newly synthesized for the present work.

## 1. Introduction

The difference in the valence between the  $B$  and  $B'$  cations in perovskite-type compounds  $A_2(BB')\text{O}_6$  and  $(AA')(BB')\text{O}_6$  is one important factor for controlling the ordering of the  $B$  and  $B'$  cations. (According to Galasso and Pyle (1), the size difference between the  $B$  and  $B'$  ions is also important.) Therefore, the electrical and magnetic properties of the compounds are strongly dependent on the valency pair  $(B, B')$ . Sleight and Weiher previously investigated the valency pair of  $(M, \text{Re})$  in ordered perovskites with the formula  $\text{Ba}_2(M\text{Re})\text{O}_6$  where  $M = \text{Mn}, \text{Fe}, \text{Co},$

and Ni (2). They showed a possibility of determining the valency pair by comparing lattice constants but their study was so inclined to the magnetic and electrical properties that they did not rationalize their method.<sup>1</sup>

In the case of  $(AA')(BB')\text{O}_6$ , where  $A$  is a bivalent cation and  $A'$  a trivalent one, there are three possibilities for the valency pair  $(B, B')$ :  $(+1, +6), (+2, +5),$  and  $(+3, +4)$ , under the requirement of electrical charge neutrality. Compounds with the formula  $(\text{SrLa})(BB')\text{O}_6$  with an ordered pair  $(+2, +5)$  for  $BB' = \text{CoNb},$

<sup>1</sup> Lattice constants of ordered perovskites  $\text{Ba}_2(MM')\text{O}_6$  listed in Table 2 in Ref. (2) provide suitable data for illustrating the present method, which determines that the valence situations are  $\text{Ba}_2(\text{Fe}^{3+}\text{Re}^{5+})\text{O}_6,$   $\text{Ba}_2(\text{Co}^{2+}\text{Re}^{6+})\text{O}_6,$  and  $\text{Ba}_2(\text{Ni}^{2+}\text{Re}^{6+})\text{O}_6.$

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CoSb, CoTa, NiNb, NiSb, NiTa, CuNb, CuSb, CuTa, and those with a disordered pair (+3, +4) for  $BB' = \text{MnTi}, \text{MnIr}, \text{FeTi}, \text{FeIr}$  were reported by Blasse (3), and the other compounds with an ordered pair (+2, +5),  $(\text{SrLa})(\text{FeTa})\text{O}_6$  (4),  $(\text{SrLa})(\text{MnW})\text{O}_6$  (5), and  $(\text{BaLa})(\text{MnMo})\text{O}_6$  (6) have been prepared in our laboratory. The investigation of the valency pair ( $B, B'$ ) is especially interesting if both  $B$  and  $B'$  have unpaired  $d$ -electrons. The valency pair ( $\text{Mn}^{2+}, \text{Mo}^{5+}$ ) in  $(\text{BaLa})(\text{MnMo})\text{O}_6$  was previously determined (6) with fluorescent X-ray Mn-K $\beta$  shifts and magnetic susceptibilities.

The present paper proposes a new method for determining the ionic valency pair of ( $B, B'$ ) in the perovskite-type compounds of  $(AA')(BB')\text{O}_6$  and  $A_2(BB')\text{O}_6$  by comparing the lattice constants of three similar compounds with known cyclic cation pairs. In order to illustrate the present method and to reexamine the valency pair of ( $\text{Mn}^{2+}, \text{Mo}^{5+}$ ) in  $(\text{ALa})(\text{MnMo})\text{O}_6$  where ( $A = \text{Ba}, \text{Sr}, \text{Ca}$ ), novel series of perovskite-type compounds  $(\text{ALa})(BB')\text{O}_6$  with cyclic cation pairs  $BB' = \text{MnMo}, \text{MoMg}, \text{MgTa}, \text{TaMn}$  were synthesized and their lattice constants were determined.

## 2. Ordered Perovskite Structure and its Lattice Constants

In compounds with the formula  $(AA')(BB')\text{O}_6$  having the cubic perovskite-type structures, the larger  $A$  and  $A'$  cations are usually distributed at random (3) among the cation sites surrounded by 12 oxygen ions and the smaller  $B$  and  $B'$  cations are orderly or randomly arranged in the octahedral cation sites surrounded by 6 oxygen ions.

Figure 1 shows the arrangement of ions in the (100) plane of the cubic perovskite structure for  $(AA')(BB')\text{O}_6$ -type compounds, where the  $B$  and  $B'$  cations are alternately arranged between oxygen ions. Holes denoted by an \* in Fig. 1 are randomly occupied by the  $A$  and  $A'$  cations. In this figure, it appears that the lattice constant  $a_0$  for an  $(AA')(BB')\text{O}_6$ -type compound is a linear function of the ionic radii of the  $B$  and  $B'$  cations,  $r(B)$  and  $r(B')$ , and for the common  $A$  and  $A'$  cations;

$$a_0 = u \cdot r(B) + v \cdot r(B') + w(A, A', O),$$

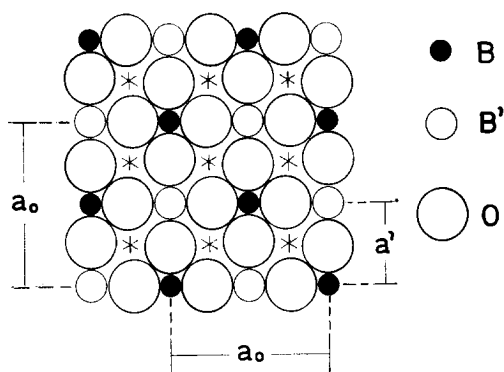


Fig. 1. Rock salt arrangement of  $B$  and  $B'$  cations in the (100) plane of the cubic perovskite structure for  $(AA')(BB')\text{O}_6$ . Lattice constant  $a_0$  and the dimension of one perovskite unit  $a'$  are shown.

where  $u, v$ , and  $w$  are parameters which depend on the ionic radii of the common  $A, A'$ , and oxygen ions. This equation is the basic hypothesis of the present method,

In order to extend the application of this linear equation to a slightly distorted perovskite structure from cubic symmetry, the  $a_0$  parameter in the linear equation is replaced by the perovskite parameter  $\bar{a}$ , defined as the cube root of the unit cell volume of  $(AA')(BB')\text{O}_6$ .

$$\bar{a} = u \cdot r(B) + v \cdot r(B') + w(A, A', O). \quad (1)$$

According to Eq. (1), the perovskite parameter of  $(AA')(BB')\text{O}_6$  with an unknown valency pair ( $\text{Mn}^x, \text{Mo}^y$ ) is given as follows.

$$\bar{a}(\text{Mn}^x, \text{Mo}^y) = u \cdot r(\text{Mn}^x) + v \cdot r(\text{Mo}^y) + w(A, A', O). \quad (2)$$

The perovskite parameters of the series of compounds,  $(AA')(\text{Mn}^{2+}\text{Ta}^{5+})\text{O}_6$ ,  $(AA')(\text{Mg}^{2+}\text{Mo}^{5+})\text{O}_6$  and  $(AA')(\text{Mg}^{2+}\text{Ta}^{5+})\text{O}_6$ , with known valency pairs, are also given by the same constants  $u, v$ , and  $w$  as those in Eq. (2), because the  $A, A'$ , and  $O$  are common ions in these compounds.

$$\bar{a}(\text{Mn}^{2+}, \text{Ta}^{5+}) = u \cdot r(\text{Mn}^{2+}) + v \cdot r(\text{Ta}^{5+}) + w(A, A', O), \quad (3)$$

$$\bar{a}(\text{Mg}^{2+}, \text{Mo}^{5+}) = u \cdot r(\text{Mg}^{2+}) + v \cdot r(\text{Mo}^{5+}) + w(A, A', O). \quad (4)$$

$$\bar{a}(\text{Mg}^{2+}, \text{Ta}^{5+}) = u \cdot r(\text{Mg}^{2+}) + v \cdot r(\text{Ta}^{5+}) + w(A, A', \text{O}). \quad (5)$$

After adding both sides of Eqs. (3 and 4), the resultant sides are subtracted by both sides of Eq. (5).

$$\begin{aligned} \bar{a}(\text{Mn}^{2+}, \text{Ta}^{5+}) + \bar{a}(\text{Mg}^{2+}, \text{Mo}^{5+}) \\ - \bar{a}(\text{Mg}^{2+}, \text{Ta}^{5+}) = u \cdot r(\text{Mn}^{2+}) \\ + v \cdot r(\text{Mo}^{5+}) + w(A, A', \text{O}), \end{aligned} \quad (6)$$

Comparing the right-hand side of Eq. (6) with that of Eq. (2), it can be seen that the perovskite parameter  $\bar{a}(\text{Mn}^x, \text{Mo}^y)$  for the unknown pair is equal to the left-hand side of Eq. (6), if the unknown pair  $(\text{Mn}^x, \text{Mo}^y)$  is  $(\text{Mn}^{2+}, \text{Mo}^{5+})$ .

$$\begin{aligned} \bar{a}(\text{Mn}^x, \text{Mo}^y) = \bar{a}(\text{Mn}^{2+}, \text{Ta}^{5+}) \\ + \bar{a}(\text{Mg}^{2+}, \text{Mo}^{5+}) - \bar{a}(\text{Mg}^{2+}, \text{Ta}^{5+}) \\ \text{only if } (x, y) = (+2, +5), \end{aligned} \quad (7)$$

This means that the unknown valency pair  $(\text{Mn}^x, \text{Mo}^y)$  in compound  $(AA')(\text{Mn}^x\text{Mo}^y)\text{O}_6$  can be determined by comparing the observed lattice constants of the series of compounds with the known cyclic ion pairs,  $(AA')(\text{Mn}^{2+}\text{Ta}^{5+})\text{O}_6$ ,  $(AA')(\text{Mg}^{2+}\text{Mo}^{5+})\text{O}_6$  and  $(AA')(\text{Mg}^{2+}\text{Ta}^{5+})\text{O}_6$ . Although some empirical ionic radii are assumed in Eqs. (1–6), they are eliminated and only the observable parameters,  $\bar{a}(\text{Mn}^x, \text{Mo}^y)$ ,  $\bar{a}(\text{Mn}^{2+}, \text{Ta}^{5+})$ ,  $\bar{a}(\text{Mg}^{2+}, \text{Mo}^{5+})$ , and  $\bar{a}(\text{Mg}^{2+}, \text{Ta}^{5+})$ , are used in the final comparison, Eq. (7). This point is important in the present method.

When the left side of Eq. (2) differs from the left side of Eq. (6) by more than the experimental error or some practical criterion for observed perovskite parameters, a further comparison of the perovskite parameters  $\bar{a}$  for the other series of compounds with known valency pairs, e.g.,  $(AA')(\text{Mn}^{3+}\text{Zr}^{4+})\text{O}_6$ ,  $(AA')(\text{Sc}^{3+}\text{Mo}^{4+})\text{O}_6$ , and  $(AA')(\text{Sc}^{3+}\text{Zr}^{4+})\text{O}_6$ , is repeated until a comparison similar to Eq. (7) agrees within the criterion.

### 3. Experimental

The perovskite-type compounds  $(AA')(BB')\text{O}_6$  that were necessary for the present work were prepared from oxides of  $\text{La}_2\text{O}_3$

(stated purity: 99.99%),  $\text{MnO}_2$  (99.9%),  $\text{MoO}_3$  (99.9%),  $\text{MgO}$  (99.9%),  $\text{Ta}_2\text{O}_5$  (99.9%),  $\text{Sc}_2\text{O}_3$  (99.9%),  $\text{ZrO}_2$  (99.8%), and  $\text{Fe}_2\text{O}_3$  (99.9%), and carbonates of  $\text{BaCO}_3$  (99.5%),  $\text{SrCO}_3$  (99.5%), and  $\text{CaCO}_3$  (99.5%). Stoichiometric mixtures of the raw materials were heated in an aluminum boat at 1100–1200°C for 1 hr under various gas atmospheres. The reacted mixtures were crushed and ground, pelletized, and reheated at 1300–1350°C for several hours in the appropriate gas atmospheres. The conditions of the final heat treatments of the compounds which we attempted to prepare in the present work are described in Table 1.

The identification of the resultant phases and the determination of the lattice constants were accomplished by a powder X-ray diffraction method with nickel-filtered  $\text{Cu-K}\alpha$  radiation (wave length = 1.5405 Å), using silicon powder (99.99%) as a standard. Lattice constants were refined by a least-squares method in a computer program RSLC-3 (7). In the case of the  $(\text{CaLa})(BB')\text{O}_6$  series, the diffraction intensity of every line was conventionally measured by cutting and weighing its profile and comparing it with the calculated one.

In order to check the ionic valence of paramagnetic ions,  $\text{Mn}^{2+}$  ( $3d^5$ ) and  $\text{Mo}^{5+}$  ( $4d^1$ ), magnetic susceptibilities of some compounds were measured in a vacuum-sealed quartz cell by a Faraday-type magnetobalance from 77 to 1200°K.

Mössbauer absorption spectra of  $(\text{SrLa})(\text{FeMo})\text{O}_6$  and  $(\text{BaLa})(\text{FeMo})\text{O}_6$  were taken at 300 and 570°K in a mixed gas ( $\text{CO}_2/\text{H}_2 = 1.26$ ) atmosphere with a source of  $\text{Co}^{57}$ , recorded with a constant-acceleration spectrometer using a multichannel analyzer. Isomer shifts were measured relative to that of the stainless steel.

## 4. Experimental Results

### 4.1. Structures from X-Ray Measurements

Despite the heat treatment of 1400°C for 10 hr, samples expected to form perovskite-type compounds of  $(\text{BaLa})(BB')\text{O}_6$  type, with  $BB' = \text{ScMo}, \text{ScZr}, \text{MnZr}, \text{FeZr}$ , were obtained as two-phase mixtures of  $\text{BaB}'\text{O}_3$  and

TABLE 1  
LIST OF THE COMPOUNDS (ATTEMPTED PREPARATION) IN THE PRESENT WORK

Compounds	Conditions in final heat treatment				Remarks
	Temperature (°C)	Time	Atmosphere		
(BaLa)(MnTa)O <sub>6</sub>	1350	4 hr	H <sub>2</sub>		single phase
(BaLa)(FeTa)O <sub>6</sub>	1350	4 hr	H <sub>2</sub> + H <sub>2</sub> O		single phase
(BaLa)(MgTa)O <sub>6</sub>	1300	8 hr	air		single phase
(BaLa)(MgMo)O <sub>6</sub>	1350	4 hr	H <sub>2</sub>		single phase
(BaLa)(FeMo)O <sub>6</sub>	1350	5 hr	H <sub>2</sub> + H <sub>2</sub> O		single phase
(BaLa)(ScMo)O <sub>6</sub>	1400	10 hr	H <sub>2</sub> + H <sub>2</sub> O		two phases
	1700	20 min	vacuum quenching		single phase
(BaLa)(MnZr)O <sub>6</sub>	1400	10 hr	air		two phases
(BaLa)(FeZr)O <sub>6</sub>	1400	10 hr	air		two phases
(BaLa)(ScZr)O <sub>6</sub>	1400	10 hr	air		two phases
	2000	20 min	vacuum quenching		single phase
(SrLa)(MnMo)O <sub>6</sub>	1350	6 hr	H <sub>2</sub> + H <sub>2</sub> O		single phase
(SrLa)(FeMo)O <sub>6</sub>	1320	5 hr	H <sub>2</sub> + H <sub>2</sub> O		single phase
(SrLa)(MgMo)O <sub>6</sub>	1350	6 hr	H <sub>2</sub> + H <sub>2</sub> O		single phase
(SrLa)(MnTa)O <sub>6</sub>	1350	6 hr	H <sub>2</sub> + H <sub>2</sub> O		single phase
(SrLa)(MgTa)O <sub>6</sub>	1350	6 hr	air		single phase
(CaLa)(MnMo)O <sub>6</sub>	1350	12 hr	Ar		single phase
(CaLa)(MgMo)O <sub>6</sub>	1350	5 hr	Ar		single phase
(CaLa)(MnTa)O <sub>6</sub>	1350	6 hr	Ar		single phase
(CaLa)(MgTa)O <sub>6</sub>	1300	10 hr	air		single phase

LaBO<sub>3</sub> compounds. Single phase (BaLa)-(ScMo)O<sub>6</sub> and (BaLa)(ScZr)O<sub>6</sub> were obtained by quenching the batches from 1700 and 2000°C, respectively, in a vacuum tungsten furnace.

All the other samples were synthesized as single phase perovskite structures for heat treatments below 1400°C as shown in Table 1. Since no diffraction lines other than those attributable to the cubic perovskite structure ABO<sub>3</sub> were found in the X-ray powder diffraction patterns of (BaLa)(BB')O<sub>6</sub> (BB' = FeMo, ScMo, ScZr) and (SrLa)(FeMo)O<sub>6</sub>, the B and B' ions (BB' = FeMo, ScMo, ScZr) are probably distributed at random among the oxygen-octahedral sites in these compounds. In other words, these compounds are mid members of the solid-solution systems of BaMoO<sub>3</sub>-LaFeO<sub>3</sub>, SrMoO<sub>3</sub>-LaFeO<sub>3</sub> ( $\delta$ ), BaMoO<sub>3</sub>-LaScO<sub>3</sub> and BaZrO<sub>3</sub>-LaScO<sub>3</sub>. While for compounds (AA')(BB')O<sub>6</sub> with BB' = MnMo, MnTa, MgMo, MgTa, and FeTa, superlattice lines caused by an ordered

arrangement of the B and B' ions in the oxygen-octahedral sites were found in the X-ray powder diffraction patterns.

For ordered compounds with the formulas (BaLa)(BB')O<sub>6</sub> and (SrLa)(BB')O<sub>6</sub>, all the diffraction lines in the patterns were indexed by a face-centered cubic unit cell with the doubled edge of the perovskite unit  $a_0 = 2a' \approx 8A$  (see Fig. 1). For ordered compounds with the formula (CaLa)(BB')O<sub>6</sub> with BB' = MnMo, MnTa, MgMo, and MgTa, on the other hand, all the diffraction lines in their powder patterns were indexed by a body-centered orthorhombic unit cell ( $a < b < c$ ) containing four monoclinic perovskite units ( $a' = c' > b'$ ,  $\beta' \neq 90^\circ$ ). Figure 2 shows a geometric correlation between the face-centered unit cell for (BaLa)(BB')O<sub>6</sub> and (SrLa)(BB')O<sub>6</sub> and the body-centered orthorhombic unit cell for (CaLa)(BB')O<sub>6</sub>, where only the B and B' ions are depicted. Indices ( $hkl$ ) and ( $HKL$ ) for (CaLa)(MgTa)O<sub>6</sub> in Table 2 are attributed to the body-centered ortho-

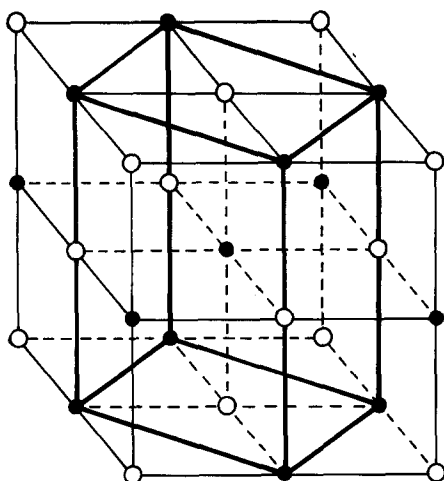


FIG. 2. Geometric connection between the face-centered unit cell for cubic  $(\text{BaLa})(\text{BB}')\text{O}_6$  and the body centered unit cell for orthorhombic  $(\text{CaLa})(\text{BB}')\text{O}_6$ . Only the  $B$  and  $B'$  ions are indicated.

rhombic cell and the face-centered (monoclinic) cell with the doubled edge of the perovskite unit, respectively. In Table 2 the observed lattice spacings and diffraction intensities of  $(\text{CaLa})(\text{MgTa})\text{O}_6$  are compared with those calculated. The intensity calculation was based on the assumptions that the  $\text{Ca}^{2+}$  and  $\text{La}^{3+}$  ions are distributed at random in the oxygen-cuboctahedral  $A$ -sites, the  $\text{Mg}^{2+}$  and  $\text{Ta}^{5+}$  ions are completely ordered over the oxygen-octahedral  $B$ -sites, and all the ions are located at their ideal positions in the perovskite structure. Agreement between the intensities is good as can be seen in Table 2. Reliability factors in this calculation were 7.1% for  $(\text{CaLa})(\text{MgTa})\text{O}_6$ , 13% for  $(\text{CaLa})(\text{MnMo})\text{O}_6$ , 7.5% for  $(\text{CaLa})(\text{MnTa})\text{O}_6$ , and 7.6% for  $(\text{CaLa})(\text{MgMo})\text{O}_6$ .

In Table 3 are listed the lattice constants and the perovskite parameters  $\bar{a}$  of the compounds synthesized in the present work, together with those of other related compounds used in later discussions.

#### 4.2. Valency States from Property Measurements

Figure 3 shows the reciprocal molar magnetic susceptibility  $\chi_m$  versus absolute temperature  $T$  for  $(\text{BaLa})(\text{MgMo})\text{O}_6$  and  $(\text{CaLa})$ -

$(\text{MgMo})\text{O}_6$ , and Fig. 4 those for  $(\text{SrLa})(\text{MnMo})\text{O}_6$  and  $(\text{BaLa})(\text{MnTa})\text{O}_6$ . Diamagnetic contribution of every ion to  $\chi_m$  was corrected according to Selwood (9). The  $\chi_m$  of  $(\text{BaLa})(\text{MgMo})\text{O}_6$  and  $(\text{CaLa})(\text{MgMo})\text{O}_6$  in Fig. 3 obey the Curie-Weiss law below room temperature with magnetic moments per Mo of  $1.6 \pm 0.05 \mu_B$  and  $1.8 \pm 0.05 \mu_B$ , respectively. These values agree within the experimental errors with the spin-only value of one unpaired electron  $1.73 \mu_B$ , showing that the molybdenum ions are in a  $\text{Mo}^{5+} (4d^1)$  state in  $(\text{BaLa})(\text{MgMo})\text{O}_6$  and  $(\text{CaLa})(\text{MgMo})\text{O}_6$ . Anomalous bends in  $\chi_m$  of these compounds above room temperature can arise from a paramagnetism caused by some electronic excitations and/or an overcorrection of diamagnetism.

The  $\chi_m$  of  $(\text{BaLa})(\text{MnTa})\text{O}_6$  in Fig. 4 obeys the Curie-Weiss Law with an effective moment of  $5.9 \pm 0.05 \mu_B$ . The  $\chi_m$  of  $(\text{CaLa})(\text{MnTa})\text{O}_6$  showed the same behaviors as that of  $(\text{BaLa})(\text{MnTa})\text{O}_6$ , obeying the Curie-Weiss law with an effective moment of  $5.9 \pm 0.05 \mu_B$ . Since the moment of spin-only value is  $5.92 \mu_B$  for the  $\text{Mn}^{2+} (3d^5)$  ion and  $4.90 \mu_B$  for the  $\text{Mn}^{3+} (3d^4)$  ion, manganese ions in  $(\text{BaLa})(\text{MnTa})\text{O}_6$  and  $(\text{CaLa})(\text{MnTa})\text{O}_6$  are in a  $\text{Mn}^{2+} (3d^5)$  state.

The  $\chi_m$  of  $(\text{SrLa})(\text{MnMo})\text{O}_6$  in Fig. 4 shows ferrimagnetic behavior quite similar to the case of  $(\text{BaLa})(\text{MnMo})\text{O}_6$  (6), with a Curie temperature of  $T_c \approx 100^\circ\text{K}$  and the asymptotic high temperature moment of  $5.9 \pm 0.05 \mu_B$  per  $(\text{SrLa})(\text{MnMo})\text{O}_6$ . Looking at the magnitudes of  $1/\chi_m$ , the contribution of the moment of the  $\text{Mo}^{5+} (4d^1)$  ion to the total moment of  $(\text{SrLa})(\text{MnMo})\text{O}_6$  will be so small that the valency pair ( $\text{Mn}^{2+}$ ,  $\text{Mo}^{5+}$ ) is safely predicted with this asymptotic moment of  $5.9 \mu_B$ . The chemical shift of the Mn-K $\beta$  line in the fluorescent X-ray observation (10) was 0.995 eV for  $(\text{SrLa})(\text{MnMo})\text{O}_6$  relative to that of the Mn metal. Since this value lies between the shift of MnO at 0.96 eV and that of  $(\text{SrLa})(\text{MnTa})\text{O}_6$  at 1.202 eV (6), the valency pair ( $\text{Mn}^{2+}$ ,  $\text{Mo}^{5+}$ ) in  $(\text{SrLa})(\text{MnMo})\text{O}_6$  is obvious.

The  $\chi_m$  of  $(\text{CaLa})(\text{MnMo})\text{O}_6$  obeyed the Curie-Weiss law above  $400^\circ\text{K}$  with a magnetic moment of  $5.7 \pm 0.05 \mu_B$ , and behaved

TABLE II  
X-RAY POWDER DIFFRACTION DATA FOR (CaLa)(MgTa)O<sub>6</sub>

<i>h k l</i>	<i>HKL</i>	<i>d</i> <sub>obs</sub>	<i>d</i> <sub>cal</sub>	<i>I</i> <sub>obs</sub> / <i>I</i> <sub>0</sub>	<i>I</i> <sub>cal</sub> / <i>I</i> <sub>0</sub>
1 0 1	1 1 1	4.5874	4.5868	31	33
0 1 1	1 $\bar{1}$ 1	4.5463	4.5462	27	32
1 1 0	2 0 0	3.9571	3.9566	5	4
0 0 2	0 0 2	3.9509	3.9505		2
2 0 0	2 2 0	2.8172	2.8166	25	25.5
1 1 2	2 0 2	2.7958	2.7956	100	100
0 2 0	2 $\bar{2}$ 0	2.7794	2.7793	23	24.6
2 1 1	3 1 1	2.3947	2.3943	18	12.7
1 0 3	1 1 3	2.3859	2.3858		6.3
0 $\bar{1}$ 3	1 $\bar{1}$ 3	2.3801	2.3800	18	6.2
1 $\bar{2}$ 1	3 $\bar{1}$ 1	2.3771	2.3770		12.4
2 $\bar{2}$ 0	4 0 0	1.9785	1.9783	43	33.9
0 0 4	0 0 4	1.9753	1.9753		11.2
3 0 1	3 3 1	1.8272	1.8269	3	2.8
2 1 3	1 3 3	1.8181	1.8179	5	5.6
1 $\bar{2}$ 3	3 $\bar{1}$ 3	1.8103	1.8103	5	5.5
0 $\bar{3}$ 1	3 $\bar{3}$ 1	1.8039	1.8039	3	2.7
3 $\bar{1}$ 2	4 2 2	1.6223	1.6221	32	20
2 0 4	2 2 4	1.6173	1.6172		9.9
0 $\bar{2}$ 4	2 $\bar{2}$ 4	1.6100	1.6100	37	9.7
$\bar{1}$ $\bar{3}$ 2	2 $\bar{4}$ 2	1.6078	1.6077		19.4
3 0 3	3 3 3	1.5291	1.5289	5	1.6
3 $\bar{2}$ 1	5 1 1	1.5268	1.5266		3.2
1 0 5	1 1 5	1.5215	1.5215	7	1.6
0 $\bar{1}$ 5	1 $\bar{1}$ 5	1.5200	1.5200		1.6
$\bar{2}$ $\bar{3}$ 1	1 $\bar{3}$ 1	1.5192	1.5191		3.2
0 $\bar{3}$ 3	3 $\bar{3}$ 3	1.5154	1.5154	5	1.6
4 0 0	4 4 0	1.4086	1.4083		5.2
2 $\bar{2}$ 4	4 0 4	1.3979	1.3978	17	20.2
0 $\bar{4}$ 0	4 $\bar{4}$ 0	1.3897	1.3896	4	4.9
4 $\bar{1}$ 1	5 3 1	1.3454	1.3452	2	2.1
3 2 3	1 5 3	1.3397	1.3396	2	2.1
2 1 5	1 3 5	1.3377	1.3376	2	2.1
1 $\bar{2}$ 5	3 $\bar{1}$ 5	1.3346	1.3346	4	2.1
2 $\bar{3}$ 3	5 $\bar{1}$ 3	1.3346	1.3345		2.1
1 $\bar{4}$ 1	5 $\bar{3}$ 1	1.3300	1.3299	2	2.06
4 $\bar{2}$ 0	6 2 0	1.2564	1.2562	3	4.3
3 $\bar{3}$ 2	6 0 2	1.2511	1.2510	10	8.6
1 $\bar{1}$ 6	2 0 6	1.2495	1.2495	10	8.5
2 $\bar{4}$ 0	6 $\bar{2}$ 0	1.2463	1.2462	3	4.2

analogous to that of (SrLa)(MnMo)O<sub>6</sub> below 300°K, but no residual magnetization was detected at 77°K. The valency pair (Mn<sup>2+</sup>, Mo<sup>5+</sup>) in (CaLa)(MnMo)O<sub>6</sub>, therefore, is not conclusive from this magnetic information.

A Mössbauer absorption spectrum of

(SrLa)(FeMo)O<sub>6</sub>, taken at room temperature, was a diffuse one made of several lines that undoubtedly came from an internal magnetic field since the compound has the Neel temperature of *T<sub>N</sub>* ≈ 450°K (8). No appreciable Mössbauer absorption, however, was detected

TABLE III

LATTICE CONSTANTS AND PEROVSKITE PARAMETERS OF PEROVSKITE-TYPE COMPOUNDS USED IN THE PRESENT WORK

Compounds	$a(\text{Å})$	$b(\text{Å})$	$c(\text{Å})$	$\bar{a}(\text{Å})$	Remarks
(BaLa)(MnMo)O <sub>6</sub>	8.119(2)			8.119(2)	(Mn <sup>2+</sup> Mo <sup>5+</sup> ) <sup>a</sup>
(BaLa)(MnTa)O <sub>6</sub>	8.173(2)			8.173(2)	— <sup>e</sup>
(BaLa)(MgMo)O <sub>6</sub>	8.009(2)			8.009(2)	— <sup>e</sup>
(BaLa)(MgTa)O <sub>6</sub>	8.057(2)			8.057(2)	— <sup>e</sup>
(BaLa)(FeTa)O <sub>6</sub>	8.150(2)			8.150(2)	— <sup>e</sup>
(BaLa)(FeMo)O <sub>6</sub>	4.003(2)	(disorder)		8.006(4)	(Fe <sup>3+</sup> Mo <sup>4+</sup> ) <sup>e</sup>
(BaLa)(ScZr)O <sub>6</sub>	4.13	(disorder)			— <sup>e,b</sup>
(BaLa)(ScMo)O <sub>6</sub>	4.05	(disorder)			— <sup>e,b</sup>
(SrLa)(MnMo)O <sub>6</sub>	8.021(2)			8.021(2)	(Mn <sup>2+</sup> Mo <sup>5+</sup> ) <sup>e</sup>
(SrLa)(MnTa)O <sub>6</sub>	8.071(3)	(corrected)		8.071(3)	— <sup>a</sup>
(SrLa)(MgMo)O <sub>6</sub>	7.928(2)			7.928(2)	— <sup>e</sup>
(SrLa)(MgTa)O <sub>6</sub>	7.973(2)			7.973(2)	— <sup>e</sup>
(SrLa)(FeTa)O <sub>6</sub>	8.013(2)			8.013(2)	— <sup>c</sup>
(SrLa)(FeMo)O <sub>6</sub>	3.955(2)	(disorder)		7.910(4)	(Fe <sup>3+</sup> Mo <sup>4+</sup> ) <sup>d</sup>
(CaLa)(MnMo)O <sub>6</sub>	5.596(2)	5.766(2)	7.976(1)	8.014(2)	(Mn <sup>2+</sup> Mo <sup>5+</sup> ) <sup>e</sup>
(CaLa)(MnTa)O <sub>6</sub>	5.597(4)	5.741(4)	7.994(2)	8.009(4)	— <sup>e</sup>
(CaLa)(MgMo)O <sub>6</sub>	5.551(1)	5.622(1)	7.875(1)	7.892(1)	— <sup>e</sup>
(CaLa)(MgTa)O <sub>6</sub>	5.558(3)	5.633(3)	7.901(2)	7.910(3)	— <sup>e</sup>

<sup>a</sup> T. Nakamura and Y. Gohshi, *Chem. Lett.* 1171 (1975).

<sup>b</sup> Lattice constants are unreliable because of some nonstoichiometry.

<sup>c</sup> T. Nakamura and T. Sata, *J. Phys. Soc. Japan* 30, 1501 (1971).

<sup>d</sup> T. Nakajima, K. Kamata, and T. Nakamura, *Bull. T.I.T.* No. 126, 19 (1975).

<sup>e</sup> Newly obtained in the present work.

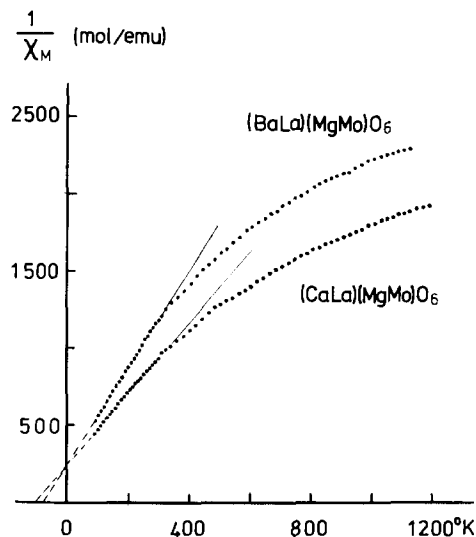


FIG. 3. Reciprocal molar magnetic susceptibility versus absolute temperature for (BaLa)(MgMo)O<sub>6</sub> and (CaLa)(MgMo)O<sub>6</sub>. Paramagnetic behavior of Mo<sup>5+</sup> below 300°K is seen.

at room temperature for (BaLa)(FeMo)O<sub>6</sub>. Figure 5 shows the Mössbauer absorption spectra of (SrLa)(FeMo)O<sub>6</sub> and (BaLa)(FeMo)O<sub>6</sub> at 570°K. A single absorption line with an isomer shift of  $IS = 0.47 \pm 0.03$  mm/sec (relative to stainless steel) and a half width of  $0.60 \pm 0.04$  mm/sec was obtained for (SrLa)(FeMo)O<sub>6</sub> but a diffuse line with  $IS = 0.62 \pm 0.04$  mm/sec was obtained for (BaLa)(FeMo)O<sub>6</sub>. These values of isomer shifts indicate a predominant presence of ferric ions Fe<sup>3+</sup> (3d<sup>5</sup>) in these compounds, i.e., the valency pair (Fe<sup>3+</sup>, Mo<sup>4+</sup>) exists in these compounds.

## 5. Discussions on the Ionic Valency Pair

The valency pair of  $B$  and  $B'$  ions in a compound  $(AA')(BB')O_6$  can sometimes be determined by means of optical spectra, Mössbauer spectra, magnetic susceptibilities, ESR spectra, etc. But the method proposed in Section

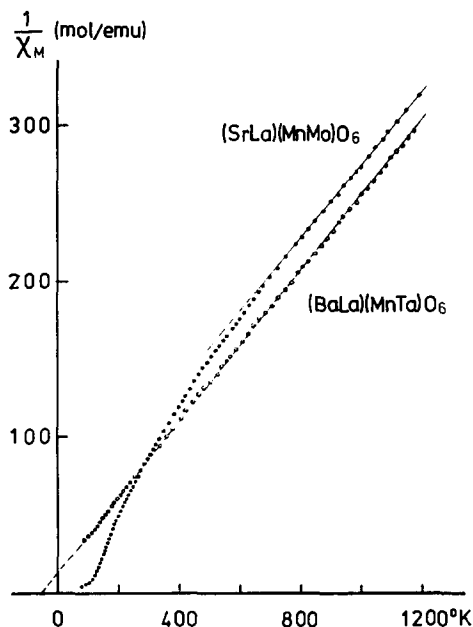


FIG. 4. Reciprocal molar magnetic susceptibility versus absolute temperature. Paramagnetic behavior for  $(\text{BaLa})(\text{MnTa})\text{O}_6$  and ferrimagnetic behavior for  $(\text{SrLa})(\text{MnMo})\text{O}_6$  are distinguished.

2 is applicable for all cases when the compounds with cyclic ion pairs ( $BB'$ ,  $B'B''$ ,  $B''B''$ ,  $B''B$ ) are present.

The accuracy in the X-ray measurement of every lattice constant in Table 3 is rather high, that is, the fluctuation accompanied by every  $\bar{a}$ -parameter is less than  $0.004 \text{ \AA}$ . The accuracy of empirical ionic radii, on the other hand, is lower of *ca.*  $\pm 0.01 \text{ \AA}$ . This implies that the size of an ion, especially for a transition-metal ion, differs from compound to compound and accompanies an uncertainty of  $\pm 0.01 \text{ \AA}$ . Therefore, we postulate here that the upper limit of fluctuation of Eq. (7) is  $0.03 \text{ \AA}$ , since the right side of Eq. (6 or 7) is an algebraic sum of two terms of transition-metal ion and one term of the other common ions.

#### 5.1. $(\text{Mn}^{2+}\text{Mo}^{5+})$ in $(\text{ALa})(\text{MnMo})\text{O}_6$ Systems

The presence of the valency pair  $(\text{Mn}^{2+}, \text{Mo}^{5+})$  in  $(\text{BaLa})(\text{MnMo})\text{O}_6$  was verified previously by means of the fluorescent X-ray Mn-K $\beta$  shift and its magnetic properties ( $\delta$ ). This result is reaffirmed by inserting the  $\bar{a}$ -parameters of  $(\text{BaLa})(\text{MnTa})\text{O}_6$ ,  $(\text{BaLa})$ -

$(\text{MgMo})\text{O}_6$  and  $(\text{BaLa})(\text{MgTa})\text{O}_6$  in Table 3 into Eq. (7). The expected parameters of  $(\text{BaLa})(\text{MnMo})\text{O}_6$  for the pair  $(\text{Mn}^{2+}\text{Mo}^{5+})$  is

$$\begin{aligned} \bar{a}(\text{Mn}^{2+}, \text{Mo}^{5+}) &= \bar{a}(\text{Mn}^{2+}\text{Ta}^{5+}) \\ &+ \bar{a}(\text{Mg}^{2+}\text{Mo}^{5+}) - \bar{a}(\text{Mg}^{2+}\text{Ta}^{5+}) \\ &= 8.173 + 8.009 - 8.057 \\ &= (8.125 \text{ \AA})_{\text{expect}}. \end{aligned}$$

This value agrees well with the observed  $\bar{a}$ -parameter of  $(\text{BaLa})(\text{MnMo})\text{O}_6$  in Table 3 within the above criterion of the fluctuation of  $0.03 \text{ \AA}$ .

$$\begin{aligned} (8.125 \text{ \AA})_{\text{expect}} &\sim (8.119 \text{ \AA})_{\text{obs}} \\ &= 0.006 \text{ \AA} < 0.03 \text{ \AA}. \end{aligned}$$

This fact again supports the presence of the valency pair  $(\text{Mn}^{2+}, \text{Mo}^{5+})$  in  $(\text{BaLa})(\text{MnMo})\text{O}_6$ .

With an analogous procedure, the expected  $\bar{a}$ -parameters of  $(\text{SrLa})(\text{MnMo})\text{O}_6$  and  $(\text{CaLa})(\text{MnMo})\text{O}_6$  for the pair  $(\text{Mn}^{2+}, \text{Mo}^{5+})$  are  $(8.026 \text{ \AA})_{\text{expect}}$  and  $(7.991 \text{ \AA})_{\text{expect}}$ , respectively. The expected parameter of  $(\text{SrLa})(\text{MnMo})\text{O}_6$  agrees well with the observed one in Table 3.

$$\begin{aligned} (8.026 \text{ \AA})_{\text{expect}} &\sim (8.021 \text{ \AA})_{\text{obs}} \\ &= 0.005 \text{ \AA} < 0.03 \text{ \AA}. \end{aligned}$$

This indicates that the valency pair  $(\text{Mn}^{2+}, \text{Mo}^{5+})$  exists in  $(\text{SrLa})(\text{MnMo})\text{O}_6$  as expected from Section 4.2. The difference in  $\bar{a}$ -parameters between the expected and the observed is not small enough for  $(\text{CaLa})(\text{MnMo})\text{O}_6$ .

$$\begin{aligned} (7.991 \text{ \AA})_{\text{expect}} &\sim (8.014 \text{ \AA})_{\text{obs}} \\ &= 0.023 \text{ \AA} < 0.03 \text{ \AA}. \end{aligned}$$

In spite of this evidence, we believe that the valency pair is  $(\text{Mn}^{2+}, \text{Mo}^{5+})$  in  $(\text{CaLa})(\text{MnMo})\text{O}_6$ . The great difference between the parameters of  $0.023 \text{ \AA}$  probably arises because of an appreciable deformation from the cubic perovskite structure in compounds  $(\text{CaLa})(\text{BB}')\text{O}_6$ .

#### 5.2. $(\text{Fe}^{3+}\text{Mo}^{4+})$ in $(\text{ALa})(\text{FeMo})\text{O}_6$

It is interesting to note that the Fe and Mo ions in  $(\text{BaLa})(\text{FeMo})\text{O}_6$  and  $(\text{SrLa})(\text{FeMo})\text{O}_6$  chose the random distribution with the



valency pair of ( $\text{Fe}^{3+}$ ,  $\text{Mo}^{4+}$ ) at the expense of the Madelung energy of 300–400 kcal/mole (11) in comparison with the case of ordered valency pair ( $\text{Fe}^{2+}$ ,  $\text{Mo}^{5+}$ ). This fact is probably caused by a special stability of the electronic state of the  $\text{Fe}^{3+}$  ion ( $L = 0$ ,  $S = \frac{5}{2}$ ), since the free energy gain from the random distribution of  $\text{Fe}^{3+}$  and  $\text{Mo}^{4+}$  is a small quantity of  $\ln 2 \cdot RT = 2.1$  kcal/mole at  $T = 1500^\circ\text{K}$ .

Similarly, the expected  $\bar{a}$ -parameters of  $(\text{BaLa})(\text{FeMo})\text{O}_6$  and  $(\text{SrLa})(\text{FeMo})\text{O}_6$  for the valency pair ( $\text{Fe}^{2+}$ ,  $\text{Mo}^{5+}$ ), if it were present, are estimated to be  $(8.102 \text{ \AA})_{\text{expect}}$  and  $(7.968 \text{ \AA})_{\text{expect}}$ , respectively, from the  $\bar{a}$ -parameters of  $(A\text{La})(B\text{B}')\text{O}_6$  where ( $A = \text{Ba}$ ,  $\text{Sr}$  and  $B\text{B}' = \text{Fe}^{2+}\text{Ta}^{5+}$ ,  $\text{Mg}^{2+}\text{Mo}^{5+}$ ,  $\text{Mg}^{2+}\text{Ta}^{5+}$ ) in Table 3. The observed  $\bar{a}$ -parameters are  $(8.006 \text{ \AA})_{\text{obs}}$  for  $(\text{BaLa})(\text{FeMo})\text{O}_6$  and  $(7.910 \text{ \AA})_{\text{obs}}$  for  $(\text{SrLa})(\text{FeMo})\text{O}_6$ . The differences between the  $\bar{a}$ -parameters are

$$(8.102 \text{ \AA})_{\text{expect}} \sim (8.006 \text{ \AA})_{\text{obs}} \\ = 0.096 \text{ \AA} > 0.03 \text{ \AA},$$

for  $(\text{BaLa})(\text{FeMo})\text{O}_6$ , and,

$$(7.968 \text{ \AA})_{\text{expect}} \sim (7.910 \text{ \AA})_{\text{obs}} \\ = 0.058 \text{ \AA} > 0.03 \text{ \AA},$$

for  $(\text{SrLa})(\text{FeMo})\text{O}_6$ . The discrepancies between the  $\bar{a}$ -parameters in these compounds are appreciably greater than the tentative criterion of 0.03 Å, indicating that the valency pair is not ( $\text{Fe}^{2+}$ ,  $\text{Mo}^{5+}$ ) in these compounds.

Because of the unfortunate lack of reliable single-phase solid solutions  $(AA')(BB')\text{O}_6$  where ( $AA' = \text{BaLa}$ ,  $\text{SrLa}$  and  $BB' = \text{FeZr}$ ,  $\text{ScMo}$ ,  $\text{ScZr}$ ), the valence check by the present method is impossible for the disordered pair ( $\text{Fe}^{3+}$ ,  $\text{Mo}^{4+}$ ). However, since  $(\text{BaLa})(\text{FeMo})\text{O}_6$  and  $(\text{SrLa})(\text{FeMo})\text{O}_6$  are the midmembers of the solid solution systems  $\text{BaMoO}_3\text{--LaFeO}_3$  and  $\text{SrMoO}_3\text{--LaFeO}_3$ , respectively, the  $\bar{a}$ -parameters expected for  $(\text{BaLa})(\text{FeMo})\text{O}_6$  at  $(7.972 \text{ \AA})_{\text{expect}}$  and for  $(\text{SrLa})(\text{FeMo})\text{O}_6$  at  $(7.908 \text{ \AA})_{\text{expect}}$  are estimated from those of  $\text{BaMoO}_3$  ( $\bar{a} = 8.080 \text{ \AA}$ ) (12),  $\text{SrMoO}_3$  ( $\bar{a} = 7.950 \text{ \AA}$ ) (12), and  $\text{LaFeO}_3$  ( $\bar{a} = 7.864 \text{ \AA}$ ) (13) on the basis of Vegard's law. Comparisons

between the estimated and the observed are

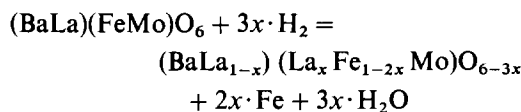
$$(7.972 \text{ \AA})_{\text{expect}} \sim (8.006 \text{ \AA})_{\text{obs}} \\ = 0.034 \text{ \AA} > 0.03 \text{ \AA},$$

for  $(\text{BaLa})(\text{FeMo})\text{O}_6$ , and,

$$(7.908 \text{ \AA})_{\text{expect}} \sim (7.910 \text{ \AA})_{\text{obs}} \\ = 0.002 \text{ \AA} \ll 0.03 \text{ \AA},$$

for  $(\text{SrLa})(\text{FeMo})\text{O}_6$ . The agreement between the estimated and the observed values is very good for  $(\text{SrLa})(\text{FeMo})\text{O}_6$ . But the estimated value for  $(\text{BaLa})(\text{FeMo})\text{O}_6$  is smaller than the observed, although it is closer than that estimated for the ordered pair ( $\text{Fe}^{2+}$ ,  $\text{Mo}^{5+}$ ).

If we suppose that Vegard's law is correct, a greater  $\bar{a}$ -value will be caused by a partial reduction of the  $\text{Fe}^{3+}$  ion into metal-Fe and will be lost from the system during the heating process in hydrogen atmosphere. Because the ionic radii  $r(\text{La}^{3+}) > r(\text{Fe}^{3+})$ , a possible mechanism for yielding a greater cell dimension is as follows.



This is consistent with a diffuse Mössbauer spectrum shown in Fig. 5 for  $(\text{BaLa})(\text{FeMo})\text{O}_6$  owing to a reduction of signal-noise ratio.

### 5.3. ( $\text{Bi}^{3+}\text{Bi}^{5+}$ ) in $\text{BaBiO}_3$

A dream of finding a  $\text{Bi}^{4+}$  ( $6s^1$ ) state, which is isoelectronic to gold  $\text{Au}^0$  in the perovskite-type compound  $\text{BaBiO}_3$  urged Nakamura et al. to investigate which of the valency states  $\text{Bi}^{4+}\text{--O}^{2-}\text{--Bi}^{4+}$  or  $\text{Bi}^{3+}\text{O}^{2-}\text{--Bi}^{5+}$  is present in  $\text{BaBiO}_3$  (14). They found no decisive evidence for the existence of  $\text{Bi}^{4+}$  in the ESR, magnetic, and electrical measurements. The charge distribution ( $\text{Bi}^{3+}$ ,  $\text{Bi}^{5+}$ ) in  $\text{BaBiO}_3$  was taken for granted by Shuvaeva and Fesenko (15), but it was denied by de Hair and Blasse (16), who compared the infrared absorption lines of  $\text{BaBiO}_3$  with those of  $\text{Ba}_2(\text{La}^{3+}\text{Bi}^{5+})\text{O}_6$  and concluded that the bismuth ions in  $\text{BaBiO}_3$  are all equivalent. Recently, Cox and Sleight have determined the crystal structure of  $\text{BaBiO}_3$  with the use of the neutron diffraction powder method (17). The structure

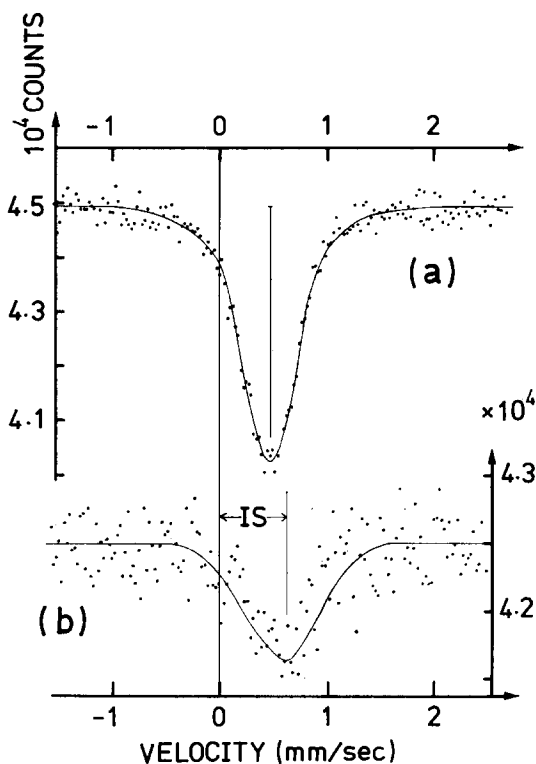


Fig. 5. Mössbauer absorption spectra for (a)  $(\text{SrLa})(\text{FeMo})\text{O}_6$  and (b)  $(\text{BaLa})(\text{FeMo})\text{O}_6$ , at  $570^\circ\text{K}$ .

has monoclinic symmetry  $I2/m$  with the constants  $a = 6.181 \text{ \AA}$ ,  $b = 6.136 \text{ \AA}$ ,  $c = 8.670 \text{ \AA}$ , and  $\beta = 90^\circ 10'$ . They found two kinds of Bi positions with different oxygen environments and concluded that the valence situation is an ordered pair ( $\text{Bi}^{3+}$ ,  $\text{Bi}^{5+}$ ). This paper also supports the ordered valency pair ( $\text{Bi}^{3+}$ ,  $\text{Bi}^{5+}$ ) in  $\text{BaBiO}_3$  as follows.

According to Section 2, the expected  $\bar{a}$ -parameter for  $\text{Ba}_2(\text{Bi}^{3+}\text{Bi}^{5+})\text{O}_6$  at  $(8.695 \text{ \AA})_{\text{expect}}$  is estimated from the cubic lattice constants of ordered perovskite-type compounds,  $\text{Ba}_2(\text{Bi}^{3+}\text{Ta}^{5+})\text{O}_6$  with ( $a = 8.568 \text{ \AA}$ ) (13),  $\text{Ba}_2(\text{Y}^{3+}\text{Bi}^{5+})\text{O}_6$  with ( $a = 8.564 \text{ \AA}$ ) (18), and  $\text{Ba}_2(\text{Y}^{3+}\text{Ta}^{5+})\text{O}_6$  with ( $a = 8.437 \text{ \AA}$ ) (2). The observed  $\bar{a}$ -parameter for monoclinic  $\text{BaBiO}_3$  (17) at  $(8.696 \text{ \AA})_{\text{obs}}$  is calculated from its lattice constants given above. A comparison of the expected  $\bar{a}$ -parameter for ( $\text{Bi}^{3+}$ ,  $\text{Bi}^{5+}$ ) with the observed is shown below.

$$(8.695 \text{ \AA})_{\text{expect}} \sim (8.696 \text{ \AA})_{\text{obs}} = 0.001 \text{ \AA} \ll 0.03 \text{ \AA},$$

Since the observed  $\bar{a}$ -parameter agrees well with the expected, the ordered valency pair ( $\text{Bi}^{3+}$ ,  $\text{Bi}^{5+}$ ) in  $\text{BaBiO}_3$  is strongly supported.

Other support of the valency pair ( $\text{Bi}^{3+}$ ,  $\text{Bi}^{5+}$ ) in  $\text{BaBiO}_3$  rests on the fact that all the other  $\text{BaB}^{4+}\text{O}_3$ -type perovskites with  $B = \text{Th}$  (19),  $\text{Ce}$  (20),  $\text{Pr}$  (20),  $\text{Tb}$  (20),  $\text{Pb}$  (21) are distorted to an orthorhombic symmetry and the unit cell contains four monoclinic perovskite units, in contrast with the fact that  $\text{BaBiO}_3$  has a monoclinic symmetry (17) and the unit cell contains four triclinic perovskite units (22).<sup>2</sup> Furthermore, the ordered perovskites

<sup>2</sup> Although no information was found in the X-ray powder pattern of  $\text{BaBiO}_3$  to suggest more than one formula unit of  $\text{BaBiO}_3$  per unit cell, Nakamura (22) inferred that  $\text{BaBiO}_3$  had a monoclinic unit cell containing four triclinic perovskite units induced by "G-type" antiparallel displacement of Ba ions "analogous to magnetic spin ordering," because of a similarity of the splittings of the originally cubic reflection lines in the X-ray powder patterns of ordered perovskites  $\text{Ba}_2(\text{La}^{3+}\text{Ta}^{5+})\text{O}_6$ ,  $\text{Ba}_2(\text{Ce}^{3+}\text{Ta}^{5+})\text{O}_6$ , and

with the formula  $Ba_2(BB')O_6$  with  $BB' = La^{3+}Ta^{5+}$ ,  $Ce^{3+}Ta^{5+}$ ,  $Pr^{3+}Ta^{5+}$ ,  $Nd^{3+}Ta^{5+}$  have a monoclinic symmetry and the unit cell contains four triclinic perovskite units (22) quite similar to  $BaBiO_3$ . These facts again support the ordered valency pair ( $Bi^{3+}$ ,  $Bi^{5+}$ ) in  $BaBiO_3$ .<sup>2</sup>

#### 5.4. ( $Bi^{3+}Sb^{5+}$ ) in $Ba_2(BiSb)O_6$

The elements bismuth and antimony have similar electronic configurations of  $6s^26p^3$  and  $5s^25p^3$ , respectively. Hence, these elements take tripositive and/or pentapositive valency states in ordinary compounds. Therefore, it is of interest to determine which one of the pairs ( $Bi^{3+}$ ,  $Sb^{5+}$ ) or ( $Bi^{5+}$ ,  $Sb^{3+}$ ) is present in  $Ba_2(BiSb)O_6$ . Since these pairs have similar electronic configurations, i.e.,  $6s^2 - 5s^0$  and  $6s^0 - 5s^2$ , with diamagnetism, the magnetic and optical methods for distinguishing these pairs can not be used. Nakamura et al. (18) previously prepared a rhombohedral-ordered perovskite  $Ba_2(BiSb)O_6$  and predicted its valency pair ( $Bi^{3+}$ ,  $Sb^{5+}$ ) by using a  $\bar{a}$ -parameter versus mean ionic radius  $\bar{r}(B, B') = \{r(B) + r(B')\}/2$  relationship for ordered perovskites  $Ba_2(BB')O_6$ .

The present method in Section 2 is more simple and straightforward than the previous one. The expected  $\bar{a}$ -parameter for  $Ba_2(Bi^{3+}Sb^{5+})O_6$  at  $(8.543 \text{ \AA})_{\text{expect}}$  is derived from the lattice constants of perovskite-type compounds  $Ba_2(Bi^{3+}Ta^{5+})O_6$  where  $(a = 8.568 \text{ \AA})$  (13),  $Ba_2(Sc^{3+}Sb^{5+})O_6$  where  $(a = 8.197 \text{ \AA})$  (13), and  $Ba_2(Sc^{3+}Ta^{5+})O_6$  where  $(a = 8.222 \text{ \AA})$  (13). The lattice constants of  $a = 8.546 \text{ \AA}$  and  $\alpha = 90^\circ 9'$  was observed for  $Ba_2(BiSb)O_6$  (18). Thus, the difference between the  $\bar{a}$ -

parameters is as follows.

$$(8.543 \text{ \AA})_{\text{expect}} \sim (8.546 \text{ \AA})_{\text{obs}} = 0.003 \text{ \AA} \ll 0.03 \text{ \AA}.$$

The results indicate that the valency pair ( $Bi^{3+}$ ,  $Sb^{5+}$ ) exists in  $Ba_2(BiSb)O_6$ .

## 6. Conclusions

Making use of a colinear arrangement of  $B$  and  $B'$  ions in perovskite-type compounds  $(AA')(BB')O_6$  and  $A_2(BB')O_6$ , a method to determine the valency pair ( $B, B'$ ) from the lattice constants of a series of compounds with cyclic ion pairs ( $B'B''$ ), ( $B''B''$ ) and ( $B''B$ ), was proposed. The method elucidated the ordered valency pairs ( $Mn^{2+}$ ,  $Mo^{5+}$ ) in  $(ALa)(MnMo)O_6$  with ( $A = Ba, Sr, Ca$ ), ( $Bi^{3+}$ ,  $Bi^{5+}$ ) in  $BaBiO_3$  and ( $Bi^{3+}$ ,  $Sb^{5+}$ ) in  $Ba_2(BiSb)O_6$ , and a disordered pair ( $Fe^{3+}$ ,  $Mo^{4+}$ ) in  $(ALa)(FeMo)O_6$  with ( $A = Ba, Sr$ ).

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$Ba_2(Pr^{3+}Ta^{5+})O_6$ , which were confirmed to have a body-centered monoclinic unit cell (similar to Fig. 2 with  $\beta \neq 90^\circ$ ) with four triclinic perovskite units (22). According to the geometric correlation, the triclinic constants (14),  $a' = b' = 4.356 \text{ \AA}$ ,  $c' = 4.333 \text{ \AA}$ ,  $\alpha' = \beta' = 89^\circ 54'$ , and  $\gamma' = 89^\circ 38'$ , give the monoclinic constants:  $a = 2a' \cos(\gamma'/2) = 6.180 \text{ \AA}$  (6.181  $\text{\AA}$ );  $b = 2a' \sin(\gamma'/2) = 6.140 \text{ \AA}$  (6.136  $\text{\AA}$ );  $c = 2c' = 8.666 \text{ \AA}$  (8.670  $\text{\AA}$ );  $\beta = \sin^{-1}(\sqrt{(1 - \cos \gamma')(1 + \cos \gamma' - 2 \cos^2 \alpha')}/\sin \gamma') = 90^\circ 8'$  ( $90^\circ 10'$ ), which agree with the values of Cox and Sleight in parentheses (17) and give the same  $\bar{a}$ -parameter within the experimental errors.

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