Preparation of the Ordered Perovskite $(SrLa)(MgMo)O_6$ and its Physicochemical Characterization

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The complex perovskite $(SrLa)(MgMo)O_6$ has been prepared at 1 350 °C under a flowing nitrogen atmosphere. The crystal system is cubic with a unit cell parameter of $a_0 = 7.932(1)$ Å. The i.r. spectrum shows two strong absorption bands at 606 and 380 cm^{-1}, respectively, which are due to $^2T_{1u}$ modes of molybdenum octahedra MoO_6 in the crystal lattice. The compound shows paramagnetic behaviour following the Curie–Weiss law below room temperature with an effective magnetic moment of 1.72(1) μ_B, which is consistent with that of the spin-only value (1.73 μ_B) for Mo^{5+} ($4d^1$ electronic configuration).

It is well known that in $A_2(BB')O_6$ and $(AA')(BB')O_6$ type perovskites an ordered distribution of two types of B and B′ ions along (111) planes is most probable when a large difference in either their charges or ionic radii exists.[1] However, an ordered arrangement of A and A′ ions on the twelve-co-ordinate site in $(AA')B_2O_6$ type perovskites is found in a very limited number of compounds.[2] The ordered valency pair (B,B′) was reported for all the compounds with the formula of $(CaLa)(BB')O_6$[3–6] where $(B^{II}B^{V})$ = (MgMo), (MgTa), (MgRu), (MgIr), (CaTa), (MnMo), and (MnTa), $(SrLa)(BB')O_6$[5–7] where $(B^{II}B^{V})$ = (MgRu), (MgIr), (MnMo), (MnTa), (FeTa), (MgTa), (CoNb), (CoSb), (CoTa), (NiNb), (NiSb), (NiTa), (CuNb), (CuSb), and (CuTa), and $(BaLa)(BB')O_6$[5,6,8–10] where $(B^{II}B^{V})$ = (MgMo), (MgIr), (MgRu), (CoRu), (NiRu), (ZnRu), (MnMo), (MnTa), (MgTa), and (FeTa).

The purpose of this study is to find out the conditions of synthesis of a new complex perovskite $(SrLa)(MgMo)O_6$, where Mg^{2+} and Mo^{5+} ions are ordered, and to characterize its physicochemical properties with various techniques such as *X*-ray diffraction, i.r. absorption spectroscopy, thermogravimetric analysis, and magnetic susceptibility measurements.

Results and Discussion

The single phase of the complex perovskite $(SrLa)(MgMo)O_6$ was obtained only in a reducing environment such as under flowing N_2 or H_2. Synthesis under the ambient atmosphere was not successful due to the formation of $SrMoO_4$[11] with the scheelite structure as a major phase where the Mo^{6+} ion is stabilized in an oxygen tetrahedron MoO_4^{2-}.

The *X*-ray powder diffraction pattern (Figure 1) indicates that $(SrLa)(MgMo)O_6$ has a perovskite structure with superlattice lines 111, 311, 331, 333, 511, and 531 implying the presence of the rock-salt arrangement (1:1 ordering) of Mg^{2+} and Mo^{5+} cations. All the diffraction lines are indexed by a face-centred cubic unit cell [lattice parameter $a_0 = 7.932(1)$ Å, double the edge of the simple perovskite]. In the Table the observed lattice spacings and diffraction intensities are compared with theoretical values. The intensity calculation was based on the assumption that the Sr^{2+} and La^{3+} ions are distributed at random in the oxygen-cubo-octahedral A sites, while the Mg^{2+} and Mo^{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 observed and calculated intensities is fairly good with a reliability factor of 8%.

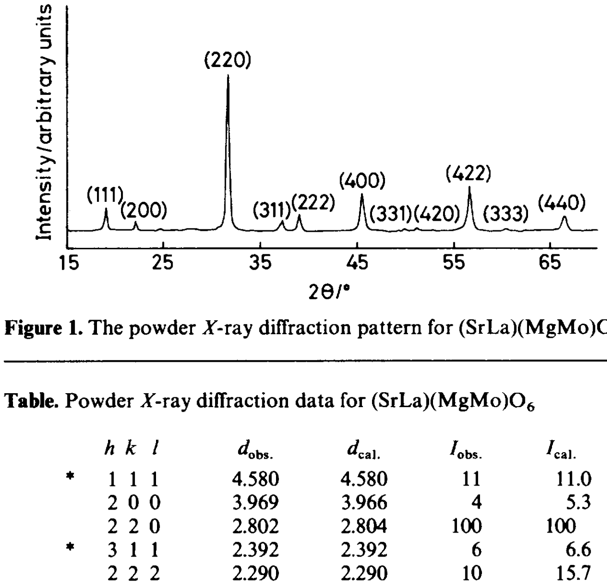

Figure 1. The powder *X*-ray diffraction pattern for $(SrLa)(MgMo)O_6$

Table. Powder *X*-ray diffraction data for $(SrLa)(MgMo)O_6$

	h k l	$d_{obs.}$	$d_{cal.}$	$I_{obs.}$	$I_{cal.}$
*	1 1 1	4.580	4.580	11	11.0
	2 0 0	3.969	3.966	4	5.3
	2 2 0	2.802	2.804	100	100
*	3 1 1	2.392	2.392	6	6.6
	2 2 2	2.290	2.290	10	15.7
	4 0 0	1.984	1.983	29	36.6
*	3 3 1	1.821	1.820	3	3.0
	4 2 0	1.776	1.774	2	2.7
	4 2 2	1.619	1.619	39	40.1
*	3 3 3	1.528	1.527	2	0.6
*	5 1 1				1.7
	4 4 0	1.402	1.402	13	21.6
	6 2 0	1.254	1.254	12	17.5

* Superlattice lines, *d* in Å.

In Figure 2 the perovskite parameter $\bar{a}$, defined as the cube-root of the cell volume of the perovskite unit, is plotted against the mean ionic radius $\bar{r} = \frac{1}{2}(r_B + r_{B'})$ for the homologous compounds of $(SrLa)(BB')O_6$, in order to check whether they have a linear relationship $\bar{a} \approx f(\bar{r})$. The ionic radii used in this plot were those given by Shannon.[12] Figure 2 indicates clearly that all the strontium compounds with an ordered valency pair of $(B^{2+}B^{5+})$ follow the linear relationship as well as $(SrLa)(MgMo)O_6$, also supporting the ordered distribution of magnesium and molybdenum ions.

In order to confirm the local symmetry of highly charged molybdenum ions stabilized in the perovskite lattice, i.r.

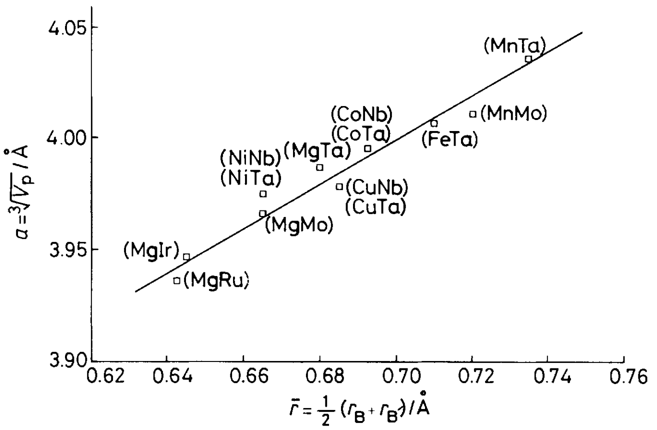

Figure 2. Perovskite parameter $\bar{a}$ *versus* mean ionic radii $\bar{r}$ for $(SrLa)(B^{2}B^{5+})O_6$

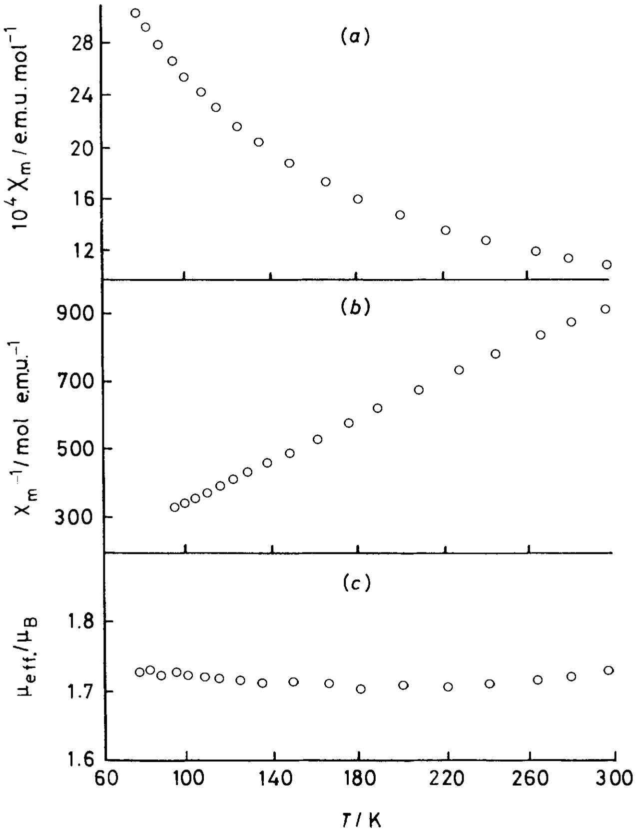

Figure 3. Temperature dependence of magnetic susceptibility χ_m (*a*), its inverse χ_m^{-1} (*b*), and effective magnetic moment $\mu_{eff.}$ (*c*) for $(SrLa)(MgMo)O_6$

absorption spectroscopic study has been performed. In ordered perovskites of the type $A_2(BB')O_6$ studied by Blasse and co-workers[13,14] the highly charged B ion octahedra like $W^{6+}O_6$, $Nb^{5+}O_6$, and $Ti^{4+}O_6$ act as independent groups. The group theoretical calculation of such BO_6 octahedron shows that the $^{2}T_{1u}$ modes are i.r.-active. In the actual i.r. spectrum of $(SrLa)(MgMo)O_6$, two strong absorption bands around 606 and 380 cm^{-1} were observed, which can be assigned to ν_3 and ν_4 modes of the MoO_6 octahedron. In addition the weak shoulder around 300 cm^{-1} might be ascribed to an external vibration.[14] From the i.r. study the local symmetry of molybdenum in the oxide lattice $(SrLa)(MgMo)O_6$ is determined to be octahedral, which confirms the result of the structural analysis.

In order to ascertain the oxidation state of the molybdenum ion in the lattice $(SrLa)(MgMo)O_6$ the magnetic susceptibility of the perovskite was measured from 77 to 300 K (Figure 3). The diamagnetic contribution of every ion to χ_m was corrected according to Selwood.[15] The χ_m values of $(SrLa)(MgMo)O_6$ obey the Curie–Weiss law below room temperature with an effective magnetic moment per molybdenum ion of 1.72(1) μ_B. The Curie constant C_m and Weiss constant θ obtained from the least-squares fit of $\chi_m^{-1} = (T - \theta)/C_m$ (T = temperature) have been estimated as 0.37 (e.m.u. K mol^{-1}) and -45.5 K, respectively. The observed moment 1.72 μ_B is consistent with the spin-only value of Mo^{5+} ($4d^1$ state), which confirms the Mo^{5+} state in $(SrLa)(MgMo)O_6$.

According to the thermogravimetric analysis of $(SrLa)(MgMo)O_6$ under an ambient atmosphere, oxygen absorption is significant above 500 °C, where a drastic mass increase is observed, which might be attributed to successive oxidation and decomposition reactions (1).

$$\begin{aligned}&(SrLa)(MgMo)O_6 + \tfrac{1}{4}O_2 \longrightarrow \\ &\quad SrMo^{6+}O_4 + MoO_3 + MgO + \text{unidentified phases} \quad (1)\\ &\quad (=SrLaMgMoO_{6.5}\text{: nominal composition})\end{aligned}$$

Even though the original perovskite phase still remained as a secondary phase in the oxidized compound, $SrMoO_4$ is easily identified as the major phase as expected. This fact also indicates that molybdenum ion is stabilized in $(SrLa)(MgMo)O_6$ in the quinquevalent state and that the compound is stable only in a reducing atmosphere at high temperature.

Experimental

The polycrystalline powder of $(SrLa)(MgMo)O_6$ was prepared by thermal decomposition of high-purity $Sr(NO_3)_2$, $La(NO_3)_3\cdot 6H_2O$, $Mg(NO_3)_2\cdot 6H_2O$, and MoO_3. The stoicheiometric mixture of the corresponding nitrates was dissolved in water and heated to obtain the oxides. The oxide mixture was ground, pelletized, and sintered in an alumina boat at 1 350 °C for several hours under a flowing nitrogen atmosphere.

The lattice constant of the resultant phase was determined by a Rigaku powder *X*-ray diffractometer with Cu-K_α radiation (λ = 1.5418 Å). The i.r. spectrum was obtained in the range 200—3000 cm^{-1}, using a CsBr pellet with a Jasco diffraction grating i.r. spectrophotometer. Magnetic susceptibility was measured with a Faraday-type magnetobalance in the temperature range from 77 to 300 K. Thermogravimetric analysis was carried out from room temperature to 1000° C under an ambient atmosphere with a Rigaku thermal analysis station Tas 100.

Acknowledgements

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