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Stabilization of Unusual Oxidation States of Chromium, Cr(IV) and Cr(V), in the Ordered Perovskite $La_2LiV_{1-x}Cr_xO_6$

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In a general study concerning the stabilization of high oxidation states in the La_2LiVO_6 matrix using high pressure, Cr(IV) (d_2) and Cr(V) (d_1), have been isolated and characterized in the double perovskites $La_2LiV_{0.90}Cr_{0.10}O_{5.95}$ and $La_2LiV_{0.90}Cr_{0.10}O_6$. Magnetic measurements and EPR study confirm such oxidation states and suggest a local tetragonal distortion of their octahedral environment in agreement with the respective $t_{2g}^2e_g^0$ [Cr(IV)] and $t_{2g}^1e_g^0$ [Cr(V)] electronic configurations. © 1994 Academic Press, Inc.

A great number of mixed metal oxides with the perovskite structure ABO_3, $A_2(BB')O_6$, $(AA')(BB')O_6$ and $A_3(BB'_2)O_9$, where B and/or B' are transition metal ions, have been prepared and studied during the last twenty years (1). Gradually it has been understood that most of the 3*d* transition metals can be stabilized as tetravalent ions to form $A^{II}B^{IV}O_3$ or $A^{II}BO_{3-x}$.

Many papers describe Cr(IV) as an unusual oxidation state but it is now known that the normal coordination for such an ion is tetrahedral with oxygen ligands under atmospheric pressure. Ba_2CrO_4, Sr_2CrO_4, Ba_3CrO_5, Na_4CrO_4, and Na_2CrO_3 have been reported as the first tetravalent chromium derivatives in the literature and recently their physical characterizations have been carried out (2–7). Attempts have also been made to stabilize Cr(IV) in an octahedral site by using the high-pressure technique. Such high-pressure conditions are able to prevent in O_h symmetry the disproportionation of Cr(IV) [(3Cr(IV) ↔ 2Cr(III) + Cr(VI)] as in CrO_2 with the rutile structure (8). Sr_2CrO_4 with K_2NiF_4 structure (9), $CaCrO_3$ (10, 11), $SrCrO_3$ (12), $BaCrO_3$ (13), and $PbCrO_3$ (14–16) with perovskite structure have been reported.

The Cr(V) ion (d^1) is also an unusual oxidation state for chromium. Due to its size, its normal coordination is tetrahedral (17–25). However, Cr(V) in near octahedral symmetry has been reported in $SrTiO_3$ by de Jong and Glasbek undergoing a static Jahn–Teller effect (26, 27). The hypothesis of small amounts of Cr(V) has been also postulated for explaining the physical properties of the solid solution $Cr_{1-x}Rh_xO_2$ (28).

In order to promote the stabilization of Cr(IV) and Cr(V), it is necessary to increase the crystal field energy at the chromium site. The La_2LiBO_6 matrix with the ordered perovskite structure was used for stabilizing Fe(V), for the first time in O_h symmetry (29). However, Fe(V) has been detected earlier by EPR in $SrTiO_3$ doubly doped with Fe and Al by Müller *et al.* (30).

In the present report our interests are focused on the stabilization of Cr(IV) and Cr(V) in octahedral sites of the perovskite $LaLiVO_6$ (V(V) being diamagnetic) (31) as $La_2LiV_{0.90}Cr(IV)_{0.10}O_{5.95}$ and $La_2LiV_{0.90}Cr(V)_{0.10}O_6$ oxides. In such a lattice, due to the 1/1 Li/V ordering the weak Li–O bond induces a strong covalency of the competing bond, and thus promotes the formation of Cr(V) as a substituting ion to vanadium(V).

EXPERIMENTAL

$La_2LiV_{0.90}Cr(IV)_{0.10}O_{5.95}$ and $La_2V_{0.90}Cr(V)_{0.10}O_6$ were prepared in three steps. First, a stoichiometric mixture of lanthanum nitrate, vanadium(V), and chromium(VI) oxides with 30% excess of lithium nitrate was calcined at about 700°C for 30 min. Excess $LiNO_3$ was added due to the low sublimation temperature of Li_2O. The second step was a heat treatment (750°C) under oxygen flow for 16 hr. Finally, a high-pressure and high-temperature treatment using a belt-type equipment (75 kbar, 900°C), was used for 10 min in order to get stoichiometric oxides. During the high-pressure synthesis of La_2LiVO_6 and $La_2LiV_{0.90}Cr(V)_{0.10}O_6$ oxygen was generated *in situ* in the belt apparatus by thermal decomposition of $KClO_3$ (32). In the high pressure cell, the remaining KCl was rapidly leached out with distilled water and absolute ethanol. The identification of the resulting phases and the determination of the lattice constants have been performed by a powder X-ray diffraction method with Ni-filtered Cu*Kα* radiation. The lattice constants were finally refined using a least-squares methods. In order to specify the valence state of chromium ions magnetic susceptibility measurements

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TABLE 1

Lattice Constants and Perovskite Parameters ($\bar{a} = \sqrt[3]{V_p}$) of La_2LiBO_{6-x} Derivatives Where B = V(x = 0), $V_{0.9}Cr^{5+}_{0.1}$(x = 0), and $V_{0.9Cr0.1}^{4+}$ (x = 0.05)

Perovskite	Lattice const. (Å)	$\bar{a}$ (Å)	Remarks
La_2LiVO_6	7.746_3	3.873	V^{5+}
$La_2LiV_{0.9}Cr_{0.1}O_6$	7.732_5	3.867	V^{5+},Cr^{5+}
$La_2LiV_{0.9}Cr_{0.1}O_{5.95}$	7.753_4	3.870	V^{5+},Cr^{4+}

were carried out with a Faraday balance from 4 to 300 K. EPR spectra were taken with a Bruker ER 2000TT X-band spectrometer (9.75 GHz) in the temperature range 10–300 K.

RESULTS AND DISCUSSION

Synthesis

Despite the heat treatment of oxygen at 700°C for 16 hr under a pressure of 0.8 kbar and at 800°C for 48 hr under 1.0 kbar, single phase with perovskite structure of La_2LiBO_{6-x} with B = V, $V_{0.90}Cr(V)_{0.10}$, $V_{0.90}Cr(IV)_{0.10}$ was observed. It seems to be only possible to prepare a single perovskite phase when the reaction mixtures were finally treated under high-pressure and high-temperature conditions (P = 75 kbar, T = 850°C). In the presence of $KClO_3$, Cr(V) was formed, without $KClO_3$ only Cr(IV) was stabilized. When the single perovskite phases were retreated in the oxygen under a pressure of order 1 kbar at approximately 800°C they were decomposed to unidentifiable mixtures. This experimental result underlines the limited stability of Cr(IV) and Cr(V) in octahedral coordination.

TABLE 3

Observed and Calculated Interplanar Spacings for $La_2LiV_{0.9}Cr_{0.1}O_6$

$h\ k\ l$	I/I_0	d_0(Å)	d_c(Å)
1 1 1	10.1	4.483	4.477
2 0 0	49.5	3.873	3.876
2 2 0	100.0	2.737	2.741
2 2 2	34.3	2.240	2.238
4 0 0	38.2	1.939	1.938
4 2 0	17.8	1.730	1.733
4 2 2	25.9	1.585	1.583
4 4 0	18.8	1.371	1.371
4 4 2	5.8	1.291	1.292
6 4 0	2.3	1.076	1.075
6 4 2	8.3	1.036	1.036

Note. a = 7.753(4) Å. The reflections of (620) (622) are overlapped with those of the Al X-ray sample holder.

X-Ray Study

The X-ray powder diffractograms indicated that La_2LiVO_6, $La_2LiV_{0.90}Cr(IV)_{0.10}O_{5.95}$, and $La_2LiV_{0.90}Cr(V)_{0.10}O_6$ have perovskite structure with superlattice lines induced by a 1/1 ordering of Li : V and Li : $V_{0.90}Cr_{0.10}$ in the octahedral B and B' sites of the double perovskite structure $A_2BB'O_6$ ($a = 2a_0 \approx 8$ Å). The refined cell parameters are given in Table 1. Tables 2, 3, and 4 show the corresponding observed and calculated d values for such pervoskite phases. Table 5 lists the lattice constants with the perovskite parameter a, defined as the cube root of the volume of perovskite unit ($a = \sqrt[3]{V_p}$) of the compounds prepared in the present work and together with those of other related La_2LiBO_6 compounds (33, 34).

TABLE 2

Observed and Calculated Interplanar Spacings for La_2LiVO_6

$h\ k\ l$	I/I_0	d_0(Å)	d_c(Å)
1 1 1	9.3	4.462	4.472
2 0 0	45.2	3.866	3.873
2 2 0	100.0	2.734	2.738
3 1 1	3.6	2.337	2.336
2 2 2	30.8	2.237	2.236
4 4 0	28.6	1.936	1.936
4 2 0	11.5	1.731	1.732
4 2 2	25.4	1.583	1.581
4 4 0	12.5	1.368	1.369
4 4 2	6.5	1.292	1.291
6 2 0	12.4	1.226	1.225
6 2 2	12.1	1.170	1.168

Note. a = 7.746(3) Å.

TABLE 4

Observed and Calculated Interplanar Spacings for $La_2LiV_{0.90}Cr_{0.10}O_{5.95}$

$h\ k\ l$	I/I_0	d_0(Å)	d_c(Å)
1 1 1	8.9	4.463	4.464
2 0 0	51.2	3.863	3.866
2 2 0	100.0	2.732	2.734
2 2 2	32.4	2.236	2.232
4 4 0	41.1	1.935	1.933
4 2 0	14.7	1.727	1.729
4 2 2	45.4	1.580	1.598
4 4 0	18.4	1.366	1.367
4 4 2	11.0	1.291	1.289
6 2 0	17.4	1.224	1.223
6 2 2	5.0	1.168	1.166
7 3 0	18.2	1.015	1.015

Note. a = 7.732(5) Å.

TABLE 5

Lattice Constants and Perovskite Parameters ($\bar{a} = \sqrt[3]{V_p}$) of La_2LiBO_6 where B = V, Fe, Ru, Os, and Ir

Perovskites	Lattice constants (Å)	Perovskite Parameters $\bar{a}$(Å)	Remarks
La_2LiVO_6	a = 7.746	3.873	(31)
$La_2LiV_{0.9}Cr_{0.1}O_6$	a = 7.733	3.867	this work (V^{5+},Cr^{5+})
$La_2LiV_{0.9}Cr_{0.1}O_{5.95}$	a = 7.740	3.870	this work (V^{5+},Cr^{4+})
La_2LiFeO_6	a = 5.371, α = 60.66° a = 7.632 (pseudocubic)	3.816	(29)
La_2LiRuO_6	a = 5.561, b = 5.597, c = 7.847	3.937	(33)
La_2LiOsO_6	a = 5.558, b = 5.654, c = 7.887	3.957	(33)
La_2LiIrO_6	a = 5.63, b = 5.58, c = 7.87	3.953	(34)

In Fig. 1, the perovskite parameter a is plotted against the ionic radii of B^{5+} ions of La_2LiBO_6 oxides. It denotes that all compounds fall on the linear relationship except La_2LiVO_6. The misfit of V^{5+} compound is approximately 0.04 Å in a, which is slightly over the experimental error limit. Such a contraction in the La_2LiVO_6 lattice might be explained if we consider the effective nuclear charge of valence electron of V^{5+} (d^0). According to the simple Slater rule, the effective nuclear charge has been estimated for the transition metal ions discussed. The d-orbital electrons of Fe^{5+} ($3d^3$), Ru^{5+}($4d^3$), Os^{5+}($5d^3$), and Ir^{5+}($5d^4$) would experience relatively smaller effective nuclear charge of Z_{eff} = 7.3 (nd^3) and Z_{eff} = 8.0 (nd^4) than that of the valence electron of V^{5+} (Z_{eff} = 11.8). Therefore, this anomalous contraction, as shown in Fig. 1, can be recognized by a shielding effect, although the relationship a vs $r(B^{5+})$ was not completely linear in terms of their ionic radii after Shannon and Prewitt (35).

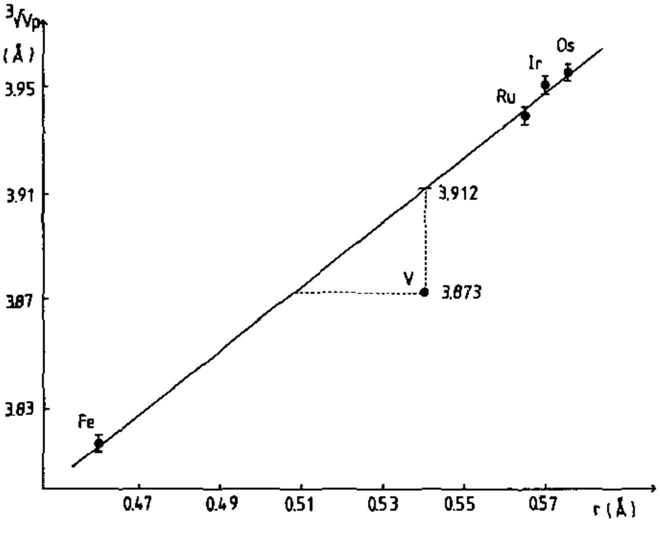

FIG. 1. The observed cubic root of perovskite cell volume ($a = \sqrt[3]{V_p}$) vs M cation radius for the series of La_2LiMO_6.

The small contraction observed by substituting V^{5+} by Cr^{5+} could be the result of a small size of Cr^{5+} ($r \approx 0.49$ Å) compared to V^{5+} (r = 0.54 Å). In the case of Cr^{4+} the slight increase (Δa = +0.007 Å) would confirm a larger ionic radius for Cr^{4+} than that for V^{5+} ($r_{Cr^{4+}}$ = 0.55 Å) the number of vacancies being negligible (one oxygen vacancy for 20 perovskite subcells).

Magnetic Measurements

The chromium-containing compounds are magnetically and isomorphously diluted in a corresponding diamagnetic matrix of La_2LiVO_6 with $V^{5+}[Ar(2d^0)]$ ions, no magnetic exchange can be expected. Figure 2 shows the reciprocal molar susceptibility χ'^{-1}_M versus absolute temperature T for $La_2LiV_{0.90}Cr(V)_{0.10}O_6$ and Fig. 3 shows that for $La_2LiV_{0.90}Cr(IV)_{0.10}O_{5.95}$ respectively. The diamagnetic contribution of every ion to χ_M was corrected according to Selwood (36).

The reciprocal molar susceptibility of Cr(V) perovskite vs T obeys the Curie–Weiss law below 60 K with a magnetic moment per chromium close to 1.734 μ_B (C = 0.375). This value agrees very well with the spin-only value of one unpaired electron (1.73 μ_B), confirming that chromium ions are in a Cr(V) ($3d^1$) state in $La_2LiV_{0.90}Cr(V)_{0.10}O_6$. The χ'^{-1}_M vs T curve for $La_2LiV_{0.90}Cr(IV)_{0.10}O_{5.95}$ prepared under 70 kbar at 900°C without oxidizing agent ($KClO_3$) also obeys the Curie–Weiss law below room temperature with an effective moment of 2.895 μ_B (C = 1.048). The spin-only moment being 2.828 μ_B for Cr^{4+}($3d^2$) ion, therefore the chromium ions in $La_2LiV_{0.90}Cr(IV)_{0.10}O_{5.95}$ oxide can be deduced as a tetravalent state in a six-coordinated site. Cr(V) and Cr(IV) ions are characterized by a T ground term $[(Cr(V):{}^2T_{2g})(Cr(IV):{}^3T_{1g})]$. The small observed spin-or-

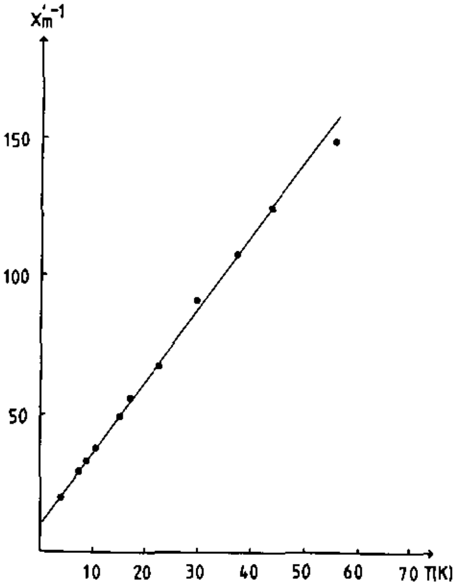

FIG. 2. Variation of the reciprocal molar susceptibility vs temperature for $La_2LiV_{0.90}Cr(V)_{0.10}O_6$.

bit contribution (the calculated effective moment being close to the theoretical one for spin-only value) could be induced by a local structural distortion of the six-coordinated chromium environment ($O_h \rightarrow D_{4h}$).

EPR Study

According to the EPR spectra of $La_2LiV_{0.90}Cr(V)_{0.10}O_6$ (after leaching of KCl with H_2O and ethanol), the asymmetry of the local environment is confirmed. It is believed to be due to the superimposition of two wide and narrow Lorentzian signals which imply that there should be two origins of paramagnetism (Fig. 4a). Both signals show anisotropy, which is mainly caused by the crystal field. The different components of the g tensor are difficult to estimate because their characterization has been carried out on powder. In order to get the exact g value of them, the samples were directly measured after the high-temperature and high-pressure treatment without KCl leaching. As shown in Fig. 4b it was possible to obtain a better resolved spectrum of $La_2LiV_{0.90}Cr(V)_{0.10}O_6$ perovskite. The intensity of the wide signal with $g = 1.85$ decreases drastically as the temperature increases and the narrow one with $g = 1.96$ was also observed to be temperature dependent. Both signals completely disappeared at room temperature even though the gain is fifty times increased (Fig. 4c).

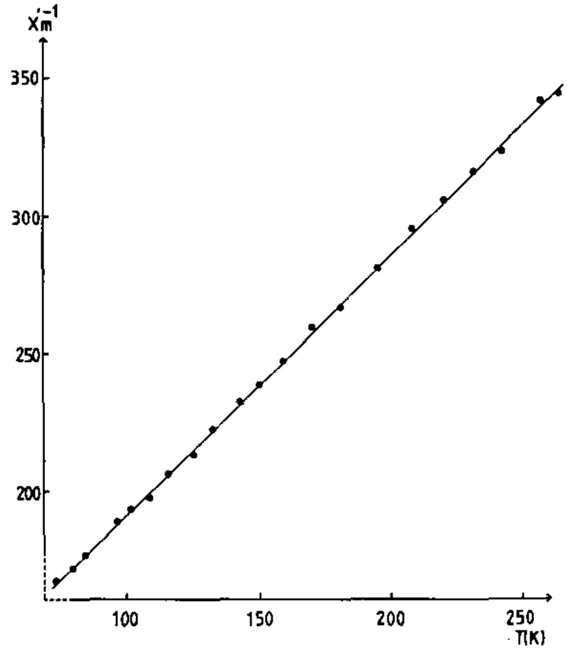

FIG. 3. Variation of the reciprocal molar susceptibility vs temperature for $La_2LiV_{0.90}Cr(IV)_{0.10}O_{5.95}$.

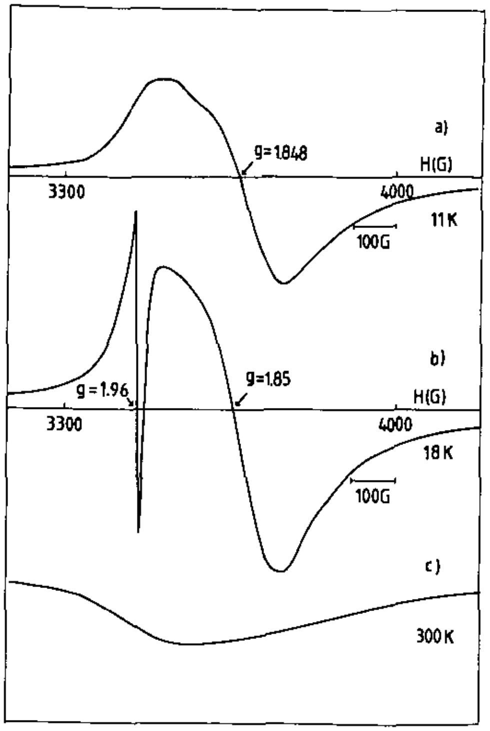

FIG. 4. EPR spectra of $La_2LiV_{0.90}Cr(V)_{0.10}O_6$. (a) after leaching of KCl with H_2O (spectrum at 11 K); (b) before leaching of KCl (spectrum at 18 K); (c) spectrum at room temperature.

For explaining the two paramagnetic origins in EPR spectrum, it might be convenient to assume first, that there are three possible paramagnetic species (V(IV), Cr(IV), Cr(V)) in the $La_2LiV_{0.90}Cr(V)_{0.10}O_6$ compound if we consider the synthetic conditions used (high temperature and high pressure).

(i) V(IV)(d^1) is one of the most widely studied ions, which is known to have a very large tetragonal component superimposed upon octahedral symmetry when the unpaired electron exists in the d_{xy} orbital. In such a strong tetragonal field, the splitting δ is so large that the relaxation time is long enough to permit the observation of EPR spectra at room tempeature (37). If the V(IV) ions exist in octahedral site of such a perovskite structure with a content of approximately 5% or less, then the hyperfine structure should also be observed even at room temperature.

(II) The Cr(IV) ions in octahedral symmetry have not been well studied but the Cr(IV) ions substituting for Al(III) in corundum illustrate the typical property of ions with an even number of electrons (38). In the corundum structure, all Al(III) ions lie along the trigonal axis of a distorted octahedron of six oxygen ions. The trigonal distortion splits the $^3T_{1g}$ ground state of Cr(IV) into an orbital singlet state A_{2g} which lies lowest and a doubly degenerate state (E_g) slightly higher. Strong spin-orbit coupling with this low lying excited state leads to a very short relaxation time and it is only possible to measure an EPR spectrum far below 4 K. Therefore, the above assumptions on the paramagnetic V(IV) and Cr(IV) can be excluded. Actually no EPR signal was observed on $La_2LiV_{0.90}Cr(IV)_{0.10}O_{5.95}$ at 10 K.

(iii) Since the $3d^1$ ions (Cr(V)) can not be detected in purely octahedral symmetry, it is, therefore, necessary to assume that the octahedral field around Cr(V) should be distorted tetragonally. Depending upon the sign of the tetragonal splitting either an orbital doublet or a singlet lies lower. In the latter case, the ground state is a spin doublet with $g_\parallel = g_\perp = g_e$, since the spin orbit coupling has been assumed to be close to zero. But even a small spin-orbit coupling completely lifts the orbital degeneracy. For the case of $O < \delta \geq \lambda$, the approximate g value can be calculated with

$$g_\parallel = g_{zz} = g_e - 8\lambda/\Delta$$

$$g_\perp = g_{zz} = g_{yy} = g_e - 2\lambda/\delta \text{ (36)}.$$

For the calculation of $g_\parallel$ value, the ligand field splitting (Δ) (approximated to 10,000 cm^{-1} for Cr(V) in tetrahedral coordination (39)) was used to estimate the ligand field splitting (Δ_0) of Cr(V) in octahedral coordination. Using on average crystal field $\Delta_0 = 22{,}500\ cm^{-1}$ and a spin-orbit coupling constant of $\lambda = 380\ cm^{-1}$ for Cr(V) (40), the calculated $g_\parallel$ value is 1.86, which is in agreement with the observed value ($g = 1.85$). Therefore, it seems evident that the most of Cr(V) ions occupies the octahedral B sites of the perovskite structure with a slight tetragonal distortion in the temperature range studied. The sharp weak resonance at $g = 1.96$ attributable to Cr(V) but in tetrahedral coordination, which was confirmed by the EPR and IR studies of oxidized catalysts of Cr_2O_3–Al_2O_3 at 77 K (17), the high-temperature solid state reaction of Cr_2O_3–V_2O_5 (19), the reactivity in the system $CuCr_2O_4$–$Cu_2Cr_2O_4$–CrO (41), and the Cr(V) in CrO doped in Ca_2PO_4Cl single crystals (20). It is therefore quite possible that a small amount of chromium (V) occupies the tetrahedral sites induced by a slight oxygen deficiency. Such a phenomenon might be energetically favored by considering the higher tetrahedral site preferential energy of Cr(V), even through the reaction was carried out at the high pressure of 75 kbar. For explaining such tetrahedral surrounding for Cr(V), in the hypothesis of a slight oxygen deficiency, an octahedral site can be transformed to a tetrahedral one if we consider a displacement of Cr(V) along a [110] direction. In fact a detailed EPR study of $SrTiO_3$ monodomain single crystal double doped with Cr and Al^{3+} has given evidence of Cr(V) ions on both octahedral (26, 27) and tetrahedral sites (42). The proportion of Cr(V) on both sites depends upon the thermal treatment.

CONCLUSION

The La_2LiVO_6 matrix being suitable for stabilizing high oxidation states of transition elements, Cr(V) and Cr(IV), have been isolated and characterized in the oxides $La_2LiV_{0.90}Cr(IV)_{0.10}O_{5.95}$ and $La_2LiV_{0.90}Cr(V)_{0.10}O_6$ with the ordered perovskite structure. The experimental and the theoretical magnetic moments, being close the oxidation states of IV and V could be confirmed. The small observed spin orbit coupling is attributable to a local structural distortion of the local octahedral sites. EPR study of Cr(V) (d^1) confirms such a slight tetragonal splitting and the possibly of some Cr(V) in tetrahedral sites.

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