

## Low-temperature preparation of some perovskites $\text{La}_2\text{MM}'\text{O}_6$ ( $\text{M}, \text{M}' = \text{Cr}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{M} \neq \text{M}'$ )\*

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**Abstract.** The low-temperature preparation of some  $\text{La}_2\text{MM}'\text{O}_6$  compounds ( $\text{M}, \text{M}' = \text{Cr}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{M} \neq \text{M}'$ ) by the decomposition of coprecipitated basic carbonates is described. Single phase compounds are formed. The stability of physical properties of these phases towards further heating depends on the M and M' ions. The results are interpreted in terms of the stability of the M-M' oxidation states.

**Keywords.** Perovskites;  $\text{La}_2\text{CrNiO}_6$ ;  $\text{La}_2\text{FeNiO}_6$ ;  $\text{La}_2\text{CrNiO}_x$ .

The low-temperature preparation methods of ceramic materials have been dealt with by several authors especially by Longo (1981) and Multani (1981). We have been regularly using such low-temperature methods for the preparation of perovskite compounds for the past few years (Madhusudhan *et al* 1980 a.) These methods involved the decomposition of coprecipitated basic carbonates. The advantage of this technique is that the diffusion of the reacting species takes place over only 50-100 unit cell dimensions, whereas in the conventional ceramic techniques the reacting species have to diffuse over distances of the order of 10,000 unit cells. Because of this the low-temperature, preparation methods are useful for the preparation of unstable phases, and also for ensuring greater homogeneity. What has not been clearly ascertained is to what extent the physical properties of such compounds prepared by low-temperature techniques correspond to those prepared by high temperature methods, and under what conditions one may expect reproducible physical properties which is independent of further heat treatment. In the preparation of  $\text{LaMO}_3$  type of compounds ( $\text{M} = 3d$  transition metal ion) we find that the low-temperature technique is enough to produce stable physical properties. However, in the case of mixed perovskites or solid solutions we find that stable physical properties are not obtained at this stage itself. In this paper we report the low-temperature preparation of  $\text{La}_2\text{MM}'\text{O}_6$  compounds ( $\text{M}, \text{M}' = \text{Cr}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{M} \neq \text{M}'$ ) and the stability of these compounds with respect to their magnetic properties on further heating. The preparation of the above mentioned  $\text{La}_2\text{MM}'\text{O}_6$  compounds has not been entirely satisfactory in earlier studies

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(Jonker 1956, 1966; Blasse 1965; Wold and Croft 1959). The x-ray diffraction lines are broad and other phases are usually present. The stability of the physical properties of the  $\text{La}_2\text{MM}'\text{O}_6$  compounds seems to depend on the nature of the M and M' ions. We have attempted to explain our observations on the basis of the recent studies of Mizushima *et al* (1979).

Approximately 0.015 M solutions of the nitrates of lanthanum and chromium and the chlorides of the cobalt, manganese, iron and nickel were prepared and the concentration of the metal ions was determined by standard gravimetric procedures to 0.1% accuracy. Stoichiometric amounts of the solutions required to give the final  $\text{La}_2\text{MM}'\text{O}_6$  composition were weighed into a beaker and the resulting solution was added drop-wise into a slight excess of 0.1 M sodium carbonate solution. The precipitate was immediately filtered and washed with water nearly twenty times till the filtrate was free from sodium ions. The basic carbonates are all insoluble in water and any loss due to washing may be considered to be negligible. The precipitate was then dried in air at 870 K and decomposed in air by slowly increasing the temperature to 1020 K. The decomposed product was ground again, pelletised and sintered for 24 hours at 1120 K. Single-phase compounds with sharp x-ray diffraction lines were obtained at this stage itself with  $\text{La}_2\text{CoMnO}_6$ ,  $\text{La}_2\text{MnNiO}_6$ ,  $\text{La}_2\text{MnCrO}_6$ ,  $\text{La}_2\text{FeCrO}_6$ ,  $\text{La}_2\text{CrNiO}_6$  and  $\text{La}_2\text{CoNiO}_6$ . It should be noted that in  $\text{La}_2\text{FeCrO}_6$  and  $\text{La}_2\text{CoNiO}_6$  the pairs  $\text{LaFeO}_3$ - $\text{LaCrO}_3$  and  $\text{LaCoO}_3$ - $\text{LaNiO}_3$  are isostructural. The most difficult ones to prepare as a single phase were  $\text{La}_2\text{CoCrO}_6$  and  $\text{La}_2\text{FeMnO}_6$ . In the latter case small amounts of what seemed to be  $\text{Fe}_3\text{O}_4$  were detected by magnetic susceptibility studies in the early stages of preparation, although x-ray diffraction did not show any extra lines. In the case of the  $\text{LaNiO}_3$ - $\text{LaFeO}_3$  solid solutions we have observed that small amount of iron ( $\sim 5\%$ ) is sufficient to remove the rhombohedral distortion of  $\text{LaNiO}_3$ . These results are surprising as earlier results have shown that the  $\text{LaFe}_{1-x}\text{Ni}_x\text{O}_3$  series prepared from the constituent oxalates or oxides show the rhombohedral structure at low concentration of iron.  $\text{La}_2\text{FeNiO}_6$  itself shows a board line x-ray diffraction pattern when the precipitate is heated at 1120 K. The nature of the diffraction pattern seems to depend on the methods of precipitation, *i.e.* stirring rate, mixing rate, etc., Different preparations give x-ray diffraction patterns which could be indexed on a tetragonal unit cell, or a cubic cell. Further heating of the samples at 1220 K for 72 hours sharpens the x-ray lines considerably in the case of  $\text{La}_2\text{FeCoO}_6$ ,  $\text{La}_2\text{CoCrO}_6$ ,  $\text{La}_2\text{FeMnO}_6$  and  $\text{La}_2\text{FeNiO}_6$ . The last compound shows a cubic perovskite structure in all cases. The traces of the  $\text{Fe}_3\text{O}_4$  impurity is also removed in  $\text{La}_2\text{FeMnO}_6$ . Further heating of the samples between 1373-1473 K for 24 hours did not show any change in the x-ray diffraction pattern.

In table 1 the symmetry of the unit cell as well as the pseudo-cubic lattice parameters are given for the  $\text{La}_2\text{MM}'\text{O}_6$  compounds after sharp x-ray diffraction lines were obtained. These are compared with the average values computed from the lattice parameters of the individual perovskites (Longo and Goodenough 1970).

We also report in table 1 the  $C$  and  $\theta$  values calculated from the slope of  $\chi^{-1}$  vs  $T$  plots obtained at different temperatures. These values are reported

Table 1. Lattice symmetry, cell parameters and magnetic properties of  $\text{La}_2\text{MM}'\text{O}_6$  compounds.

Compound	Symmetry <sup>†</sup>	Pseudo-cubic cell parameter (Å)		Magnetic properties				
		Observed	calculated <sup>a</sup>	Temperature range (°K)	$\theta$ (°K)	C		
						observed	calculated	
		Spin	Spin	Spin	Spin	Spin	Spin	
$\text{La}_2\text{CrMnO}_6$	O	3.88	3.887	> 600	52	4.88	4.88	4.07
$\text{La}_2\text{CeFeO}_6$	O	3.90	3.904	> 550	-500	5.49	6.26	6.46
$\text{La}_2\text{CrCoO}_6$	R	3.85	3.860	> 300	-825	3.69	4.87	5.68
$\text{La}_2\text{CrNiO}_6$	O	3.88	3.869	> 500	-195	2.86	2.24	1.65
$\text{La}_2\text{MnFeO}_6$	O	3.89	3.914	> 250	45	5.07	7.38	4.38
$\text{La}_2\text{MnCoO}_6$	O	3.89	3.897	340-550	240	5.60	6.00	5.60
				> 550	350	3.40	(3.74)*	(5.61)*
$\text{La}_2\text{MnNiO}_6$	O	3.87	3.887	> 300	300	3.18	3.37	1.57
$\text{La}_2\text{FeCoO}_6$	R	3.88	3.890	> 500	-650	6.80	(2.87)*	(3.98)*
$\text{La}_2\text{FeNiO}_6$	C	3.89	3.897	> 750	-	6.08	7.38	9.99
$\text{La}_2\text{CoNiO}_6$	R	3.86	3.850	-	-	-	4.75	5.95

a) From Longo and Goodenough (1970). The pseudo-cubic cell parameter of

$\text{La}_2\text{MM}'\text{O}_6$  is calculated to be the average of  $\text{LaMO}_3$  and  $\text{LaM}'\text{O}_3$

\* Calculated for  $\text{M}^{+2} - \text{M}'^{+2}$

† O-orthorhombic; R-Rhombohedral; C-Cubic

for the  $\text{La}_2\text{MM}'\text{O}_6$  compounds after the final stages of heating and are compared with the values calculated assuming spin-only contributions, as well as spin + orbit contributions. The values seem to show that the ions are in 3+ oxidation state in all cases with sizable orbital contributions.

In the initial stages of heating the  $\chi_m^{-1}$  vs  $T$  plots are different from those of the final stages of heating. Even though sharp x-ray diffraction lines are obtained, only  $\text{La}_2\text{MnCoO}_6$  and  $\text{La}_2\text{MnNiO}_6$  shows reproducible magnetic susceptibility values which are independent of further heat treatment. In all other cases the magnetic susceptibility values change with firing temperature and reaches a steady value only at the final stages. The  $\chi_m^{-1}$  vs  $T$  plots of some of the representative compounds after the first stage of heating and after the magnetic properties have stabilised are shown in figure 1. In the initial stages of heating, the values obtained at high temperatures are different from those reported in table 1. This shows that although single-phase compounds are obtained by the low-temperature decomposition, chemical inhomogeneities are present which probably accounts for the broad x-ray diffraction lines. At low temperatures of firing there are probably  $\text{LaMO}_3$ -rich and  $\text{LaM}'\text{O}_3$ -rich regions and only firing at high temperatures removes these chemical inhomogeneities.

It would be pertinent to consider the energy levels of the M and M' ions in various oxidation states. Mizushima *et al* (1979) have estimated the energy levels for the iron group ions in  $\text{TiO}_2$  based on photo-current measurements. As a first approximation it seems reasonable to assume that the same stability conditions are qualitatively applicable to the same ions in the corresponding perovskites. We may therefore use the results of Mizushima *et al* to consider the energies of the  $\text{M}^{+3}\text{-M}'^{+3}$ ,  $\text{M}^{+4}\text{-M}'^{+2}$  and  $\text{M}^{+2}\text{-M}'^{+4}$  with respect to the valence band in  $\text{TiO}_2$  and apply the same criterion to the perovskites. The results are shown in table 2. We note from table 2 that the  $\text{M}^{+4}\text{-M}'^{+2}$  pairs are more stable for the Mn-Co and Mn-Ni pairs while the  $\text{M}^{+3}\text{-M}'^{+3}$  pairs are more stable in Fe-Ni, Fe-Co and Fe-Cr pairs.

Since a charge difference ordering potential favours the ordering of the M and M' ions into different sublattice we expect that where such charge difference potential exists, the  $\text{La}_2\text{MM}'\text{O}_6$  compounds would be readily formed and exhibit stable physical properties. This accounts for the ease of formation and the stability of  $\text{La}_2\text{MnCoO}_6$  and  $\text{La}_2\text{MnNiO}_6$  compounds. We expect a similar ordering in  $\text{La}_2\text{CrNiO}_6$  and  $\text{La}_2\text{CrCoO}_6$  and the magnetic susceptibility studies show these compounds to exhibit ferrimagnetic type of behaviour at low temperatures. In the case of  $\text{La}_2\text{FeCoO}_6$ ,  $\text{La}_2\text{FeCrO}_6$  the  $\text{M}^{+3}\text{-M}'^{+3}$  pairs are more stable. There may not be any charge difference potential for their ordering and the M and M' ions may be randomly distributed. This random ordering of the M and M' ions has important consequences especially in percolation problems and we shall present data in this regard in a subsequent paper.

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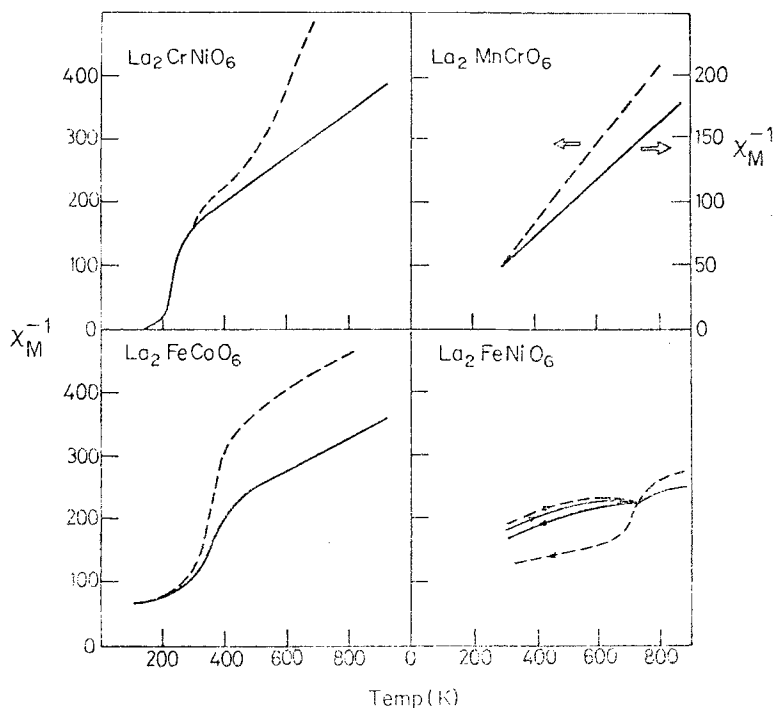


Figure 1.  $\chi_M^{-1}$  vs  $T$  plots of some  $\text{La}_2\text{MM}'\text{O}_6$  compounds. Dotted line indicate the values obtained after the first heating. Full lines indicate the values obtained after the susceptibility values do not change on further heating. The  $C$  values for the stabilised phases are given in table 1.

Table 2. Energy of  $\text{MM}'$  pairs in  $\text{TiO}_2^a$

M	M'	Total energy (in eV) <sup>b</sup>		
		$\text{M}^{+3} - \text{M}'^{+3}$	$\text{M}^{+4} - \text{M}'^{+3}$	$\text{M}^{+2} - \text{M}'^{+4}$
Cr	Mn	2.6	2.1	2.8
Cr	Fe	0.8	2.9	4.8
Cr	Co <sup>c</sup>	1.3	2.2	4.3
Cr	Ni	0.4	1.0	-
Mn	Fe	2.0	1.3	2.3
Mn	Co <sup>c</sup>	2.6	0.3	1.8
Mn	Ni	1.6	-0.9	-
Fe	Co <sup>c</sup>	0.7	1.9	3.1
Fe	Ni	-0.2	0.7	-

(a) Mizushima *et al* (1979)

(b) Energy measured from the top of the valence band

(c) The  $\text{Co}^{+4}$  levels have been taken as  $-0.6$  eV by extrapolation of the results of Mizushima *et al* (1979).

discussions especially with respect to the stability of the M and M ions. He would also like to thank Mr N Y Vasanthacharya for some help in measurements. He would also like to acknowledge the valuable support and encouragement of Professor C N R Rao.

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