Determination of average oxidation state of Mn in ScMnO₃ andCaMnO₃by using iodometric titration

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ABSTRACT

The compounds $ScMnO_3$ and $CaMnO_3$ were obtained by high- temperature solid state reactions considering a stoichiometric rate of $CaCO_3$: Mn_2O_3 and Sc_2O_3:Mn_2O_3. The findings were characterized by X-ray powder diffraction. The determination method of average oxidation state of these compounds based on dissolving the samples in concentrated HCl solution. Cl_2 obtained by dissolving the samples is reduced by KI solution. I_2 was titrated with standard sodium thiosulfate solution. In the calculation it was taken α as a fraction of Mn^{3+} in the mixed oxides. The formula of Scandium manganite was formulated as $ScMnO_{3+0.12}$, and for calcium manganite as $CaMnO_{3-0.03}$. The relative standard deviation in the identification of Mn does not exceed 3,5%.

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تحديد متوسط درجة الأكسدة للمنغنيز في
$ScMnO_3$ و $CaMnO_3$ بالمعايرة اليودية

رياض طلي

قسم الكيمياء ــ كلية التربية بصلالة ــ صلالة ــ سلطنة عمان

الملخص

اصطُنع في هذا البحث المركبان $ScMnO_3$ و $CaMnO_3$ بهدف تعيين متوسط درجة الأكسدة للمنغنيز في كل منهما، وقد استُعملت طريقة المعايرة اليودية لتحديد كمية كل من Mn^{3+} و Mn^{4+} فـــي كـــل مـــن المركبين، ومنه حُسب عدد ذرات الأوكسجين الداخل في كل صيغة، وقد أعطت الحسابات النهائية الـــصيغ الدقيقة الآتية: $ScMnO_{3+0.12}$ و $CaMnO_{3-0.03}$ بانحراف قياسي نسبي لا يتجاوز 3.5% .

الكلمات المفتاحية: متوسط درجة أكسدة المنغنيز في $ScMnO_3$ و $CaMnO_3$.

Introduction

For many years mixed oxides of manganese have found a great interest among researchers, due to the specific structure, physical and chemical properties.

Mixed –valence manganese oxides $(R_{1-\alpha} A_\alpha)$ MnO_3 where (R: three-valence transition element, A: Alkali or Alkaline earth cation), with a structure similar to Perovskite $CaTiO_3$ exhibits a rich variety of electronic and magnetic phases. Several schemes have been proposed for dealing with changing the magnetoresistance when the oxidation state of manganese is changed.

In some papers it was shown that unoccupied orbitals of oxygen in $LaMnO_3$ and $CaMnO_3$ are substantially hybridized with the 3d orbital of Mn in the covalent bond [1]. The solid solution $(R_{1-\alpha}A_\alpha)$ MnO_3 shows a giant magnetic resistance and has an electroconductivity and catalytic effect in the oxide-reoxidation. Ferromagnetic oxides with Mn in a mixed –valence state seem to be good candidates to show magnetoresistance. The discovery of giant magnetoresistance [2,3] in mixed oxides of manganese has stimulated the research of this property in related compounds.

The oxygen's content and oxidation state of chemical formula is related to a partial content of cation- replacement, synthetic conditions and determination of sample[4]. References include identification data of oxygen content in manganese mixed oxides from results of magnetic parameters, thermographymetric analysis and other physical methods. But chemical analytical methods with reliable exactness for these compounds are almost absent.

The main aim of this paper is to adopt a method for identification of average oxidation state of manganese in mixed oxides using chemical analysis. In the current study we report the synthesis of $CaMnO_3$ and $ScMnO_3$ and the determination of oxidation state of Mn using iodemetric method in addition to other methods such as structure determination[5]. This kind of compounds was chosen because of its structural similarity with known mineral Perovskite

$CaTiO_3$. On the other hand, these compounds have a specific magnetic and electric properties.

Experimental part

Compounds used in this study were obtained by high-temperature solid state reactions taking a stoichiometric rate of $CaCO_3$: Mn_2O_3 and Sc_2O_3: Mn_2O_3. The specimens were grounded in graphite mortar by adding the acetone as a useful material for obtaining homogenous mixture. Then using the compressor the samples were pressed into tablet forms, and placed in a porcelain crucible and heated at $1100C^0$ for 20 hours in air. After that the samples were removed and regrounded for 5 minutes and heated again in the same temperature for 12 hours [6,7]. The findings were characterized by x-ray powder diffraction using Diffractometre Philips-1840 (CuK_α) as shown in fig.1[8,9,10,11].
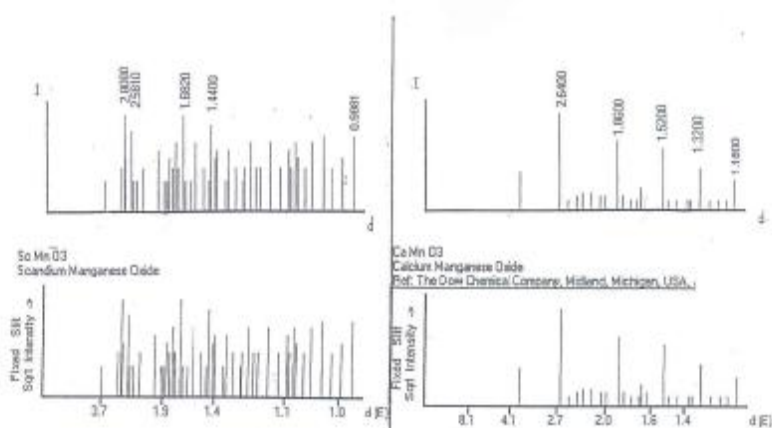
Fig.1. X-ray powder pattern for ScMoO₃ and CaMnO₃ (above), and their comparison with references(below).

All used chemicals were of analytical reagent grade (Pro-analysis). For realization of experiment, the following solutions were used:
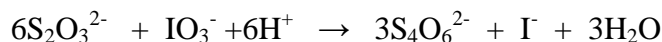
Concentrated solution of HCl.

An aqueous solution of 20% KI.

1% solution of starch.

An aqueous solution of (0,01M) sodium thiosulfate $Na_2S_2O_3.5H_2O$.

The sodium thiosulfate has been standardized by standard solution of (0.01M) KIO_3 with starch indicator according to the equation:

$$6S_2O_3^{2-} + IO_3^- + 6H^+ \rightarrow 3S_4O_6^{2-} + I^- + 3H_2O$$

Setting the experiment

Mixed oxides are relatively weakly dissolved in acids, so we decided to pound the samples before the analysis to shorten the time of dissolving. The experiment includes three parts as shown in fig.2: Flask No.1 for dissolving sample ($ScMnO_3$ or $CaMnO_3$) in concentrated HCl, it has 2 joint stopcocks, one of which for flowing N_2 which will carry Cl_2 produced from dissolving the sample through the other joint to flask No.2 which contains KI solution. Besides, to avoid the reaction between KI and air oxygen we divided the process to two separate flasks. Part No.3 is the bottle containing N_2. Nitrogen, which is an inert gas, is bubbled through the solution system for two purposes:

I) to get rid of Cl_2 .

II) to generate an inert atmosphere in the reaction vessel.
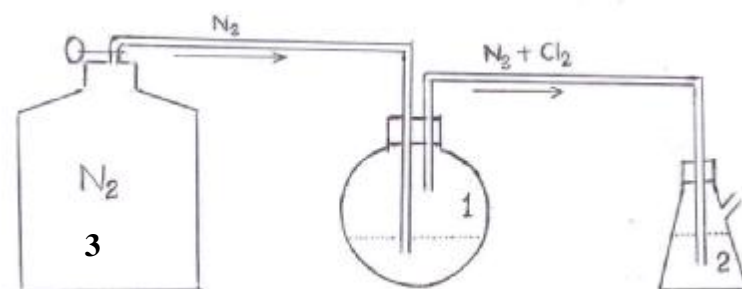
**Figure.2.Apparatus for the determination of average oxidation state of Mn.**
  1- flask for dissolving the sample in concentrated HCl.
  2- flask contains KI solution.
  3- Bottle contains N_2.

Results and discussion

The analysis of mixed oxides containing Mn is very difficult because of the transformation of samples into solution state, also being the manganese in different oxidation states [12,13]. The design of current method based on dissolving the samples in concentrated HCl solution according to the following two reactions:

$$Mn^{3+} + Cl^- \rightarrow Mn^{2+} + 1/2Cl_2$$
$$Mn^{4+} + 2Cl^- \rightarrow Mn^{2+} + Cl_2$$
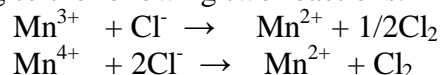
Then Cl_2 is moving to the flask No.2 where 20% KI solution is; therefore, chlorine is reduced from 0 in Cl_2 to −1 in KCl, and iodide is oxidized from −1 in KI to 0 in I_2 as in the equation:

$$Cl_2 + 2I^- \rightarrow I_2 + 2Cl^-$$
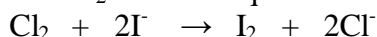
Overabundant amount was taken from KI solution in comparison with stoichiometric ratio for complete. dissolving of I_2.

I_2 is titrated with standard sodium thiosulfate solution according to the equation:

$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$$
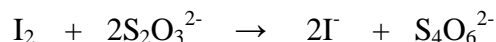
Last reaction will be following using a starch /iodine indicator, the end point occurs when the bluish-black color of the indicator disappears to give a colorless solution.
On the other hand Cl_2 might be dissolved in H_2O according to the equation:

$$Cl_2 + H_2O \rightarrow HCl + HClO$$
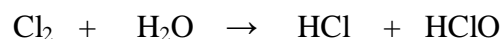
But the dissolving of Cl_2 in water is near zero at 80 C^o, so the reaction was heated to 80 C^o .

Identification of average oxidation state of Mn in ScMnO₃ and CaMnO₃

For this aim about 20 − 30 mg (precisely weighted 0,1mg) was taken from ScMnO₃ and finely grounded. Next the sample was placed in a flask No.1 and about 20 ml concentrated HCl was added and heated to about 70 −80 C^o. The sample was dissolved at the same time

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with flowing of N_2 from bottle.3. Therefore, the produced Cl_2 with N_2 go to flask No.2 which contains 10 ml of 20% solution KI .

Dissolving of sample at the temperature of $70 - 80\ C^o$ continues until we notice the solution containing the sample transforms to colorless state completely. Then we continue the heating for few minutes until the whole Cl_2 goes to flask 1 .

After that the solution in flask No.2 was transmitted into conical flask(capacity 100 ml) and titrated with standard (0,01M) sodium thiosulfate solution using 1% starch solution as an indicator.

The above mentioned procedure was repeated for the second compound $CaMnO_3$.

Analytical results of samples $ScMnO_3$ and $CaMnO_3$ are presented in tables 1 and 2 .

In the current work it was taken α as a fraction of Mn^{3+} in the mixed oxides $ScMnO_3$ or $CaMnO_3$, then $1-\alpha$ = the fraction of Mn^{4+}, so due to the equation of dissolving we can write the following:

$$\frac{m}{M}\left[\,\alpha\ +\ 2\,(\,1-\alpha\,)\,\right]\ =\ V.C$$

which leads to: $\alpha = 2 - \dfrac{V.C.M}{m}$

M:molecular weigh of the studied compound ($ScMnO_3$ or $CaMnO_3$).
C: concentration of sodium thiosulfate (mole/ lit).
m: weigh of the sample ($ScMnO_3$ or $CaMnO_3$), mg.
V: volume of thiosulfate solution (ml) used in the iodometric titration.

Our experiment presents a precision quantities for α .

For exactness of results we used the following factors :

$$\overline{a}\ =\ \frac{1}{n}\sum_i \alpha_i \qquad\qquad \text{the average value of } Mn^{3+}.$$

$$S = \sqrt{\frac{\sum_i (a_i - \overline{a})^2}{n-1}} \qquad\qquad \text{standard deviation.}$$

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$$S_r = \frac{s}{\overline{a}} \times 100\%$$ relative standard deviation.

$$\overline{a} \pm \frac{t\,S}{\sqrt{n}}$$ confidence interval.

Table.1.Determination of quantity Mn^{3+} in $ScMnO_3$.

Sample	m(mg)	V (ml) (0.01M) $Na_2S_2O_3.5H_2O$	a
1	29.5	24.62	0.766
2	29.0	24.20	0.766
3	27.2	22.73	0.764
4	27.7	23.22	0.760
5	27.3	22.82	0.764
Average	28.1	23.52	0.764

Table.2.Determination of quantity Mn^{3+} in $CaMnO_3$.

Sample	m (mg)	V(ml) (0.01M) $Na_2S_2O_3.5H_2O$	a
1	24.8	33.80	0.051
2	23.3	31.81	0.048
3	21.8	29.69	0.052
4	25.5	34.81	0.048
5	24.0	32.71	0.051
Average	23.9	32.56	0.050

The number of oxygen atoms exists in the compound related with the amount of Mn^{3+} and Mn^{4+}. For the first compound the number of oxygen atoms =

$$\frac{Sc\,oxidation\,state + \left(\overline{a}\times 3\right) + \left(1-\overline{a}\right)4}{2}$$

The number of oxygen atoms in the second compound =

$$\frac{Ca\,oxidation\,state + \left(\overline{a}\times 3\right) + \left(1-\overline{a}\right)4}{2}$$

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The result shows that the $ScMnO_3$ has the following parameters :

$$\bar{a} = 0.764 \qquad S = 0.0024 \qquad S_r = 0.31\%$$

$$\bar{a} \pm \frac{t\,S}{\sqrt{n}} = 0.764 \pm 0.0023$$

($t = 2.132$ at the 95% confidence interval, degrees of freedom $n\text{-}1 = 4$)

The confidence interval shows that the number of Oxygen atoms falls within the range :

$$\bar{a} + \frac{t\,S}{\sqrt{n}} \qquad \text{——} \qquad \bar{a} - \frac{t\,S}{\sqrt{n}}$$

By substituting the appropriate values in the formulas above we get oxygen atoms in the range 3.119 __ 3.117 which are approximated to 3.12 (3+0.12).

For the second compound $CaMnO_3$, the following parameters were calculated :

$$\bar{a} = 0.050 \qquad S = 0.0019 \qquad S_r = 3.5\%$$

$$\bar{a} \pm \frac{t\,S}{\sqrt{n}} = 0.050 \pm 0.0018$$

($t = 2.132$ at the 95% confidence interval, degrees of freedom $n\text{-}1 = 4$)

The range of oxygen atoms extents from $\bar{a} + \dfrac{t\,S}{\sqrt{n}} \quad \text{——} \quad \bar{a} - \dfrac{t\,S}{\sqrt{n}}$

(2.976 __ 2.974) which was approximated to 3- 0.025 (3 - 0.03) .

[The 95% confidence interval was selected for all experiments performed. This level was chosen because a 5% error is generally analytically acceptable.]

So due to the above results, the formula of scandium manganite derived can now be formulated as:

$$ScMnO_{3+0.12}$$

And the formula of calcium manganite can be written as:

$$CaMnO_{3\text{-}0.03}$$
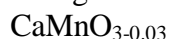
For the estimation of accuracy of results, the pure sample from Mn_2O_3 has been analysed and led to the parameters listed in the table.3.

Table.3. Analytical results of sample Mn$_2$O$_3$.

Weigh of the sample Mn$_2$O$_3$ (mg)	Mn contained in the sample(mg)	Mn calculated in the sample (mg)
25.6	17.2	17.8
28.5	19.3	19.8
29.8	20.2	20.7
26.9	18.4	18.7
27.2	18.6	18.9

Table.3 shows that the experimental quantities are in close agreement with the calculated values. According to the results obtained by our procedure, the relative standard deviation in the identification of Mn does not exceed 3.5%.

Conclusion

Iodometric titration was used for determination of average oxidation state of Mn in ScMnO$_3$ and CaMnO$_3$ compounds. The number of oxygen atoms that exists in the compound was calculated based on the amountof Mn^{3+} and Mn^{4+}. The final calculations presented the formula: ScMnO$_{3+0.12}$ and CaMnO$_{3-0.03}$ .This method allows to indicate the average oxidation state for other complicated manganites with relative standard deviation not going beyond 3.5%.

REFERENCES

1. **Advanced in physics, 1999, vol. 48, No. 2, 67 – 293.**
2. **Physical Review. (1999). B 59, 8748-8788.**
3. **Moukovski, Y. M, Russ, J. (2001). Chem. Obsh. Mendeleev, v. 9, No. 5-6.**
4. **Lurie,U.U. (1989). Reference in analytical chemistry, Moscow.**
5. **Dyachenko, O. G., Tabachenko, V. V., Tali, R., Kovba, L. M., Marinder, B. O., Sudberg, M. (1996). Structure of UMoO5 Studied by Single-Crystal X-ray Diffraction and High-Resolution Transmission Electron Microscopy- Acta Cryst. B52, 961-965.**
6. **Corneluis, A. L., and Light, B. E. (2003). Evolution of the magnetic ground state in the Electron- Doped Antiferrmagnetic CaMnO$_3$, Cond-mat/28 may. Vol. 3.**
7. **Ausloos, M., Hubert, L., Dorbdo, S., Gilabert,A., and Cloots, R. (2003). J.Cond-mat ,Vol.1.**
8. **Wang, Z. L., Yin, J. S., and Jiang, Y. D. (2000). Micron (31), 571- 580.**
9. **Qian, Q., Tyson, T. A., and others. (2000). Journal of Physics and Chemistry Solids (61), 457- 460.**
10. **X-ray powder pattern of CaMnO$_3$, Ref: The Dow Chemical Company, Midland, Michigan, USA, Private Communication. (1996).**
11. **X-ray powder pattern of ScMnO$_3$, Ref: Komissarova, Inorg. Mater. (Engl. Trasl.), 2, 236 (1996).**
12. **Crasicova, M. V. (2002). J. Physical Technology, Vol.72, (5), 30- 38.**
13. **Tretyakov, Y. D., Gudilin, E. A., Perishkov, D. V., and Etkis, D. M. (2004) Russian Academy of Science, Uspechi Khymi, 73 (4), 954-973.**