# Preparation and X-ray Powder Diffraction Study of the Pyrochlores CdLn(TiSb)$O_7$ (Ln = Nd, Gd, Yb) and $Na_{0.5}Ln_{1.5}$(TiSb)$O_7$ (Ln = Nd, Sm, Gd, Dy, Yb)*

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Cubic non-deficient $A_2B_2O_7$ pyrochlores constitute a wide family of compounds whose crystal structure can be described in the space group $Fd\bar{3}m$, $Z = 8$. If the centre ($\bar{3}m$) is chosen as origin, the large A cations occupy 16(c) positions (0, 0, 0); the smaller B cations are located at 16(d) (½, ½, ½); and the oxygen atoms are in two kinds of positions: 8(a) (1/8, 1/8, 1/8); and 48(f), ($x$, 1/8, 1/8), with only one variable positional parameter, $x$.

The large variety of cations that are allowed to occupy the A and B positions explains the great number of known compounds of this structural type [1]. A or B positions are frequently occupied by two or more cations at random. In several cases this occurs for both A and B positions, the cations only having to satisfy the charge neutrality condition. Thus, compounds of stoichiometry $A^{II}A^{III}(B^{III}B^{VI})O_7$ or $A^{II}A^{III}(B^{III}_{0.5}B^{V}_{1.5})O_7$ are known [2].

This work describes the preparation of two new families of pyrochlores, $A^{II}A^{III}(B^{IV}B^{V})O_7$ and $A_{0.5}{}^{I}A_{1.5}{}^{III}(B^{IV}B^{V})O_7$, and reports on their structural data.

## Experimental

CdLn(TiSb)$O_7$ samples were prepared from stoichiometric mixtures of analytical grade CdO, $Ln_2O_3$ (Ln = Nd, Gd, Yb), $TiO_2$ and $Sb_2O_3$. As for $Na_{0.5}Ln_{1.5}$(TiSb)$O_7$ samples, mixtures of $Na_2CO_3$, $Ln_2O_3$ (Ln = Nd, Sm, Gd, Dy, Yb) were prepared using a slight excess (10%) of $Na_2CO_3$, so as to offset the partial volatilization of the alkaline element. In every case the mixtures were ground and heated in air at 923, 1073 and 1274 K for 24 h each, and at final temperatures of 1523 K for the Cd compounds or 1393 K for those of Na, also for 24 h. After each thermal treatment the materials were quenched, weighed, ground and examined by X-ray diffraction.

Details of the analysis of the X-ray diffraction data and collection of intensities have been described elsewhere [3]. The calculation of the intensities for each compound was performed as indicated in ref. 3 for the values of the oxygen positional parameter $x = 0.410, 0.411, ..., 0.430$. The $x$ value chosen was the one leading to a smallest discrepancy $R$ factor between observed, $I_o$, and calculated, $I_c$, intensities,

$$R = \Sigma|I_o^{1/2} - I_c^{1/2}|/\Sigma I_o^{1/2}$$

where $I_o = kI'_o$, and $k = \Sigma I_c/\Sigma I_o$.

## Results and Discussion

CdLn(TiSb)$O_7$ and $Na_{0.5}Ln_{1.5}$(TiSb)$O_7$ were obtained as pale coloured powders, yellow for the three Cd compounds, grey for that of Na/Nd and yellowish white for the remaining Na compounds. All of them gave good X-ray diffraction patterns, characteristic of cubic pyrochlores, space group $Fd\bar{3}m$ (No. 227), $Z = 8$. The unit-cell parameters are given in Table I.

In both families of compounds a regular decrease in the $a$ values is observed when the mass of Ln

TABLE I. Structural Data for the Pyrochlores CdLn(TiSb)$O_7$ and $Na_{0.5}Ln_{1.5}$(TiSb)$O_7$ (Unit-cell parameters and M–O distances in Å)

| A | $a$ | $x$ | $R$ | A–$O_o$ | A–$O_o$ | B–$O_o$ | B–$O_c$ |
|---|---|---|---|---|---|---|---|
| CdNd | 10.2916(2) | 0.424 | 0.051 | 2.47 | 2.48 | 1.98 | 1.98 |
| CdGd | 10.2414(1) | 0.423 | 0.037 | 2.45 | 2.46 | 1.97 | 1.98 |
| CdYb | 10.1617(3) | 0.421 | 0.030 | 2.42 | 2.42 | 1.97 | 1.98 |
| $Na_{0.5}Nd_{1.5}$ | 10.3332(3) | 0.424 | 0.028 | 2.48 | 2.51 | 1.99 | 1.98 |
| $Na_{0.5}Sm_{1.5}$ | 10.2597(3) | 0.423 | 0.049 | 2.46 | 2.48 | 1.98 | 1.98 |
| $Na_{0.5}Gd_{1.5}$ | 10.2467(4) | 0.421 | 0.047 | 2.45 | 2.46 | 1.98 | 1.98 |
| $Na_{0.5}Dy_{1.5}$ | 10.2151(1) | 0.418 | 0.046 | 2.42 | 2.45 | 1.99 | 1.98 |
| $Na_{0.5}Yb_{1.5}$ | 10.1585(3) | 0.416 | 0.035 | 2.40 | 2.41 | 1.99 | 1.98 |

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increases. This correlates with the size diminution of the rare earth elements.

The best discrepancy $R$ factors were obtained for Cd or Na and Ln randomly distributed; (1:1) or (1:3) at 16(c) positions; Ti and Sb occupying statistically 16(d) positions, and oxygen at 8(a) and 48(f), with the positional $x$ parameters that are indicated in Table I, where final $R$ factors are also included.

The observed distances $A-O_o$ and $B-O_o$ of Table I agree with those calculated for the sums of Shannon ionic radii [4], $A-O_c$ and $B-O_c$.

The gradual variation of the oxygen positional $x$ parameter can be derived from the decrease of the A–O distances from Ln = Nd to Ln = Yb.

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