NEW SERIES OF Te⁶⁺-CONTAINING GARNETS

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NEW SERIES OF Te6+-CONTAINING GARNETS

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For hexavalent tellurium, as also for Sb5+, a strong preference for 6-coordination is characteristic in oxide compounds (1). Te-containing compounds are known with the spinel structure (2, 3), perovskite structure (4), etc. Recently, garnets of the type `{A$_{3}$$^{2+}$}[Te$_{2}$$^{6+}$](B$_{3}$$^{2+}$)O$_{12}$`* were synthesized, where A = Ca, Cd and B = Zn, Co (5). It was shown by X-ray diffraction that the Te6+ ions ($r = 0.56$ Å**) in these compounds also have 6-coordination, displacing the considerably larger Zn2+ (0.74 Å) and Co2+ (0.72 Å) ions into tetrahedra. We studied the replacement in Te-garnets of divalent ions by mono- and trivalent ions.

The starting components of the charge were $CaCO_3$, Na_2CO_3, oxides of rare-earth elements Y_2O_3, Fe_2O_3, Al_2O_3, Sb_2O_3, (extra pure), Bi_2O_3, Ga_2O_3 (analytical grade), and TeO_2 (pure). The pressed mixtures were slowly heated (3-5 h) in air and held at the specified temperature for 5-10 h. During the process

Table 1

Conditions of preparation and characteristics of garnets `{A$_{3}$}[Te$_{2}$$^{6+}$](B$_{3}$)O$_{`

Composition	Stability range, °C	Lattice constant, a_0, Å	X-ray density, g/cm^3	Powder color
$Na_3Te_2Fe_3O_{12}$	725-775*	12.386 ± 3	4.778	Brick-red
$Na_3Te_2Ga_3O_{12}$	750-800	12.358 ± 3	5.104	White
$Na_3Te_2Al_3O_{12}$	700-800*	12.188 ± 4	4.247	Same
$Pr_3Te_2Li_3O_{12}$	750-1150	12.606 ± 2	5.906	Light green
$Nd_3Te_2Li_3O_{12}$	700-1100	12.556 ± 2	6.046	Lilac
$Sm_3Te_2Li_3O_{12}$	700-1100	12.465 ± 2	6.302	Light cream
$Eu_3Te_2Li_3O_{12}$	700-1100	12.427 ± 2	6.393	White
$Gd_3Te_2Li_3O_{12}$	750-1100	12.391 ± 2	6.560	Same
$Tb_3Te_2Li_3O_{12}$	750-1050	12.346 ± 2	6.667	» »
$Dy_3Te_2Li_3O_{12}$	700-1050	12.307 ± 2	6.807	» »
$Ho_3Te_2Li_3O_{12}$	700-1050	12.271 ± 2	6.930	Yellow

Composition	Stability range, °C	Lattice constant, a_0, Å	X-ray density, g/cm^3	Powder color
$Er_3Te_2Li_3O_{12}$	750-1000	12.236 ± 2	7.030	Pink
$Tu_3Te_2Li_3O_{12}$	750-975	12.204 ± 2	7.122	White
$Yb_3Te_2Li_3O_{12}$	700-975	12.173 ± 2	7.267	Same
$Lu_3Te_2Li_3O_{12}$	750	12.150 ± 2	7.352	» »
$Y_3Te_2Li_3O_{12}$	750-1050	12.267 ± 2	5.286	» »
$Bi_3Te_2Li_3O_{12}$	700	12.600 ± 3	7.269	» »
$CaGd_2Sb_2Zn_3O_{12}$	1150-1250	12.623 ± 2	6.511	» »
$Ca_3Te_2Zn_3O_{12}$	750-1150	12.579 ± 2	5.094	» »
		12.58 (5)		

* The garnet is not single-phase.

upon heating, Te4+ and Sb3+ were oxidized to Te6+ and Sb5+. The sintered samples were studied for phase composition (URS-50IM diffractometer, CoKα radiation), and the lattice constant was determined. Table 1 gives the temperature ranges for the synthesis of single-phase ceramic garnets. At tempera-

* Ions occupying the *c*-, *a*-, and *d*-positions in the structure, with coordination numbers 8, 6, and 4, respectively, are enclosed in braces, square brackets, and parentheses.
** Ionic radii according to Ahrens for coordination number 6.

at 25-50° above the upper boundary of the synthesis region, the garnets are unstable and decompose. It is possible that the true decomposition limits of a number of garnets lie somewhat lower, and that decomposition of the garnets would be observed upon increasing the duration of the experiments.

Upon substitution according to the scheme $A^{2+} + B^{2+} \rightarrow Na^{+} + B^{3+}$, garnets of the type $\{Na_3\}[Te_2](B_3^{3+})O_{12}$ with $B = Fe, Ga, Al$ were obtained. Since 4-coordination for Fe^{3+}, Ga^{3+}, and Al^{3+} in the garnet structure presents no difficulties, there is no reason to suppose that the distribution differs from that given. Low decomposition temperatures (800-825°) and comparatively narrow temperature regions of synthesis are characteristic of Na garnets. $Na_3Te_2Fe_3O_{12}$ and $Na_3Te_2Al_3O_{12}$ could not be obtained completely single-phase.

Li^{+} is the only monovalent ion that can occupy *d*-positions in the garnet structure (cryolithionite $\{Na_3\}[Al_2] \cdot (Li_3)F_{12}$ and its analogues (^{6})). In our case, paired with $Li^{+}(d)$, rare-earth ions from Pr^{3+} to Lu^{3+}, as well as Y^{3+} and Bi^{3+}, enter the *c*-positions, forming garnets of the type $\{Ln_3^{3+}\} \cdot [Te_2](Li_3)O_{12}$. In these garnets Te^{6+} also must occupy the *a*-positions. The 6-coordination of Te^{6+} ions is confirmed by the fact that, from a mixture corresponding to the composition $Na_2CaLi_2Te_3O_{12}$, a garnet (with 1/3 of the tellurium in tetrahedra) is not formed. Thus, we have the first example of 4-coordination of Li^{+} in the structure of oxide garnets. In known Li-containing oxygen garnets Li^{+} occupies *a*-positions (^{7}).

Fig. 1. Lattice constants a_0 as a function of the atomic number of Ln^{3+}, N, for garnets: 1 $-Ln_3Ga_5O_{12}$ (7), 2 $-Ln_3Te_2Li_3O_{12}$

Figure 1: Fig. 1. Lattice constants a_0 as a function of the atomic number of Ln^{3+}, N, for garnets: 1 $-Ln_3Ga_5O_{12}$ (7), 2 $-Ln_3Te_2Li_3O_{12}$

Fig. 1. Lattice constants a_0 as a function of the atomic number of Ln^{3+}, N, for garnets:
1 $-Ln_3Ga_5O_{12}$ (7), 2 $-Ln_3Te_2Li_3O_{12}$

$Bi_3Te_2Li_3O_{12}$ is the first garnet in which all c-positions are occupied by Bi^{3+} ions. In the system $Y_{3-x}Bi_{xFe}5O_{12}$, $x_{\max} = 1.5$, and extrapolation gives for the hypothetical $Bi_3Fe_5O_{12}$ a lattice constant $a_0 = 12.621$ Å (8), located approximately midway between the values of the parameters of the hypothetical garnets $Pr_3Fe_5O_{12}$ (12.646 Å) and $Nd_3Fe_5O_{12}$ (12.600 Å) (9). In Te—Li garnets, Bi^{3+} is much closer in size to Pr^{3+} than to Nd^{3+}, although the difference between the parameters of the Pr and Nd garnets (0.050 Å) is practically the same as for ferrite garnets (0.046 Å).

Most Te—Li garnets can be obtained single-phase over a wide temperature interval. In the series of rare-earth garnets (including yttrium), the decomposition temperatures decrease with decreasing size of the c-ions. Of the rare-earth garnets, only the lutetium garnet cannot be obtained single-phase in experiments of short duration; however, when the synthesis time is increased to 20 h (750°), the $Lu_3Te_2Li_3O_{12}$ ceramic is practically single-phase. $Bi_3Te_2Li_3O_{12}$, in accordance with the low melting temperature of Bi_2O_3 (825°), is more low-temperature and decomposes already at 750°.

It is interesting to compare the isomorphous capacity of Te—Li and Ga garnets ($Ln_3Ga_5O_{12}$), which have similar lattice constants (Fig. 1). In (10) we emphasized the great influence of the strength of metal—oxygen bonds in the tetrahedral sites of the lattice on the isomorphous capacity and ease of formation of garnets. The strength of the Li^+—O^{2-} bonds is considerably less than that of Ga^{3+}—O^{2-}, i.e., the structure of Te—Li garnets is more flexible. Therefore, although the tetrahedral voids in Te—Li garnets are occupied by larger ions ($r_{Li^+} = 0.68$ Å) than the octahedral ones, which is unfavorable from the spatial point of view, the isomorphous capacity with respect to rare-earth elements of both types of garnets is the same.

In the series of Te—Li garnets the parameter increases with increasing size of Ln^{3+} faster than in other known types of rare-earth garnets ($\mathrm{Ln_3Fe_5O_{12}}$, $\mathrm{Ln_3Ga_5O_{12}}$, $\mathrm{Ln_3Al_5O_{12}}$ (7), $\mathrm{Ln_3Co_{2.5}Ge_{2.5}O_{12}}$ (11)) (see Fig. 1). Since the Li^+ $-\mathrm{O}^{2-}$ bonds are weak and the structure is flexible, the rare-earth ions occupy the c-positions "comfortably" : the larger Ln^{3+} ions push apart the O^{2-} ions, increasing the volume of the dodecahedra, whereas the smaller ions, conversely, contract the dodecahedra. In the flexibility of their structure the Te—Li garnets approach hydrogarnets, in which, for example, large Sr^{2+} ions (c) and small

Al^{3+} ions (a) can "coexist" —a combination impossible for anhydrous garnets (^{10}).

It is probably from the viewpoints set forth above that one can explain the fact that $Bi_3Te_2Li_3O_{12}$ exists and its Ga analogue is absent. The pliability of the lattice makes it possible to adapt the shape and dimensions of the dodecahedra to the crystallochemical individuality of Bi^{3+}, whereas in the more rigid lattice of Ga garnets such matching is no longer realized.

Garnets of the type $\{A_3^{2+}\}[Te_2](Zn_3)O_{12}$ are formed because the tetrahedra contain large, low-charged Zn^{2+} ions (0.74 Å), i.e., the metal—oxygen bonds are weakened. However, the structure obtained is strained and the isomorphous capacity is small. Only Ca^{2+} (0.99 Å) and Cd^{2+} (0.97 Å) enter the c-positions, but with Sr^{2+} (1.12 Å) a garnet is not formed. More than half of Zn^{2+} can be replaced by Co^{2+} (0.72 Å), but with Co^{2+} alone (and likewise with Ni^{2+} (0.69 Å) and Mg^{2+} (0.66 Å)) a garnet is not formed. The author did not succeed in obtaining garnets of the type $Ln_3^{3+}Te_{4/5}^{5}M_{1/5}^{2+}O_{12}$ (M = Zn, Co). An attempt to synthesize garnets with Be^{2+} (0.35 Å) in the d-positions was unsuccessful with A = Ca, Cd, Mg.

One more new garnet with $Zn^{2+}(d)$ can be obtained by blocking the a-positions with Sb^{5+} ions—$\{CaGd_2\}[Sb_2](Zn_3)O_{12}$. With Co^{2+} a similar garnet is not formed.

For several Te garnets a chemical analysis for tellurium was performed (analyst S. A. Malyutin). The analysis showed the absence of Te^{4+} and a content of Te^{6+} in $Ca_3Te_2Zn_3O_{12}$ of 33.87 wt.% (calculated 33.42), in $Gd_3Te_2Li_3O_{12}$ of 27.60% (calculated 27.16%), and in $Y_3Te_2Li_3O_{12}$ of 34.59% (calculated 34.73%). According to V. I. Sokolov' s data, in $Yb_3Te_2Li_3O_{12}$ and $Er_3Te_2Li_3O_{12}$ no magnetic ordering is observed above 1.5°K. Apparently, the Néel points of Te—Li garnets, as also of rare-earth Ga garnets, are located below 1.5°K.

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Note added in proof. Substitution by mono- and trivalent ions only in the c- and d-positions is also possible. Garnets $\{Na_{1.5}Gd_{1.5}\}[Te_2](Zn_3)O_{12}$ and $\{Ca_3\}[Te_2](Li_{1.5}Ga_{1.5})O_{12}$ were synthesized at 800 and 900° respectively and have parameters 12.606 ± 0.005 Å and 12.468 ± 0.002 Å.

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Note: Figure translations are in progress. See original paper for figures.