of Mg or Al between the tetrahedral and octahedral sites is almost constant against Ga content in the MgAl$_2$O$_4$ solid solution. A compositional variable of the Ga/(Mg+Ga) ratio in the octahedral site is not influenced by the occupancy of Al. The occupancy of Al is independent of the occupancy of Ga, though it depends on the occupancy of Mg according to thermal history. The local Al-O bond length in the tetrahedral site is 0.15 Å longer than the expected bond length. The nature that Al in spinel structure occupies mainly the octahedral site arises from the character of Al itself.

Keywords: spinel, crystal structure, NMR spectroscopy

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**Soft synthesis and crystallographic characterization of calcium magnesium mixed carbonates**

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It seems to be generally accepted that smithsonite, magnesite, siderite, as well as mixed carbonates like dolomite (MgCaCO$_3$) or huntite (Mg$_{0.75}$Ca$_{0.25}$CO$_3$) have been formed in the nature under hydrothermal conditions. Rao et al. developed a general soft synthesis procedure for obtaining anhydrous carbonates by precipitation from solution at normal pressure. They had success in the synthesis of smithsonite and siderite, but failed in the magnesite synthesis. This finding questions that the hydrothermal synthesis were the only way of genesis of some of these minerals in nature. The scope of this work is to apply the Rao et al. method to the synthesis of double carbonates of general formula Mg$_x$Ca$_{1-x}$CO$_3$. The compounds obtained have been characterized by X-ray fluorescence, atomic absorption analysis, TG and X-ray powder diffraction. The results obtained clearly demonstrate that anhydrous double calcium magnesium carbonate minerals can be obtained by soft synthesis for x composition ranging from 0 to 0.7. Hydroxysalts instead of anhydrous salts are obtained for larger values of x. The crystallographic parameters of the anhydrous compounds have been calculated and it has been shown that the volume of the cell accomplishes with the Vegard law.

Keywords: alkaline-earth double carbonates, lattice parameters

**P10.05.37**


**Olivine from highly oxidized scoria and lava of Kasayama volcano, Hagi, Japan**

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Oxidation state and distribution of Fe in olivine, M2M12O$_{19}$, in the anedetic scoria and lava oxidized at high temperature were investigated using FeL$_3$/FeL$_2$-intensity ratio, X-ray Rietveld and $^{57}$Fe Mössbauer methods. Olivine samples were collected from the reddish black and black scorias, and the reddish black and black Opx-andesites in Kasayama volcano, Hagi, Yamaguchi Prefecture. The Fo contents of olivine in reddish scoria exceeded 91 mol%, while those of reddish black and black scorias are 83-85 and 79-81mol%, respectively. The Fe$^{2+}$/Fe$^{3+}$ ratios in olivine of reddish black and black scoria determined using FeL$_3$/FeL$_2$-intensity ratio are Fe$^{2+}$/Fe$^{3+}$ = 92(3)-93(3):8(3)-7(3) and Fe$^{2+}$/Fe$^{3+}$ = 93(3)-98(3):7(3)-1(3), respectively. The Fe$^{2+}$/Fe$^{3+}$ ratios in olivine of reddish black and black scoria oxidized at high temperature were investigated using FeL$_3$/FeL$_2$-intensity ratio, X-ray Rietveld and $^{57}$Fe Mössbauer methods. Olivine samples were collected from the reddish black and black scorias, and the reddish black and black Opx-andesites in Kasayama volcano, Hagi, Yamaguchi Prefecture. The Fo contents of olivine in reddish scoria exceeded 91 mol%, while those of reddish black and black scorias are 83-85 and 79-81mol%, respectively. The Fe$^{2+}$/Fe$^{3+}$ ratios in olivine of reddish black and black scoria determined using FeL$_3$/FeL$_2$-intensity ratio are Fe$^{2+}$/Fe$^{3+}$ = 92(3)-93(3):8(3)-7(3) and Fe$^{2+}$/Fe$^{3+}$ = 93(3)-98(3):7(3)-1(3), respectively. On the other hand, the Fe contents of olivine in reddish black and black scoria were 91-99, 79-80 and 73-80, respectively. The Fe$^{2+}$/Fe$^{3+}$ ratios in olivine of reddish black and black scoria are 92(3)-99(3):8(3)-1(3) and 93(3)-99(3):7(3)-1(3), respectively. Mg and Fe occupancies at M1 and M2 in olivine refined by the X-ray Rietveld method (Rwp=4.89, Re=3.79, S=1.29) are Mg(M1)=0.835 (7), Fe(M1)=0.165 (7), Mg(M2)=0.830 (6), Fe(M2)=0.170 (6). The $^{57}$Fe Mössbauer spectrum of olivine in the reddish black scoria consists of three doublets which are assigned to Fe$^{2+}$(M1,M2) and Fe$^{3+}$(M1,M2) in olivine and Fe$^{2+}$(M1,M2) in laths. The Fe$^{2+}$(M1,M2):Fe$^{3+}$(M1,M2) ratios determined by $^{57}$Fe Mössbauer spectroscopy in the black scoria is Fe$^{2+}$/Fe$^{3+}$=69:31, and the resulting chemical formula of the olivine is [Mg$_{0.835}$Fe$_{0.165}$]$^{2+}$O$_{4}$, although the amount of
Oxidation state and distribution of Fe in pumpellyite from Chichibu belt, Ozu, Ehime, Japan

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Crystal structure of chromian pumpellyite was analyzed using Fe Mössbauer and chemical analysis, the resulting Mössbauer method is 20(2):80(2). The Mössbauer doublet of Fe2+ has an intensity of the Fe X-ray lines. The resulting Mössbauer analysis of the Fe content of the pumpellyite is 97.462(3). Rietveld refinements gave Fe(II):Fe(III) = 998.14(7) Å. The unit cell parameters a = 19.1614(8) Å, b = 5.9393(2) Å, c = 19.1927(6) Å, β = 998.14(7) Å. Rietveld refinements gave Fe(X):Fe(Y) ratio of 43:57. By applying the Fe2+/Fe3+ ratio determined by the Mössbauer method, the Fe content of the pumpellyite is 71-065, Poland, 2Institute of Physics PAS, AL Lotnikow 32/46, 02-668 Warszawa, Poland, E-mail: jablom@pro.onet.pl

Keywords: pumpellyite, chromium, crystal chemistry

Phase composition of natural ilmenites used in white pigment production

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Ilmenites as a natural source of titanium oxide are widely used in pigments production. TiO2 is produced mainly by sulphate method, where reaction of titanium raw material with sulphuric acid is the first step of the process. Knowledge about the phase content and the ionic states of elements in ilmenites is fundamental to proper adjustment of the chemical reactions. The origin of the minerals influence the composition through the distribution of main phases and minority elements and thus have a large influence on efficiency, safety, kinetics of reaction and the quality of products. Due to complicated morphology of these minerals standard procedures used in industrial’s chemical analysis provides the element content in form of common oxides. This is far away from real phase content and ionic state. We present the studies of ilmenites from Norway, China, Australia and India. The main phases which involve Fe and Ti as well as minor elements like Mg, Mn and Cr. In some of the minerals minor elements we found in more than one phase. This work was partially supported by European Community under Contract RII3-CT-2004-506008 (IA-